Department of Energy
Washington DC 20545

September 22, 1987

MEMORANDUM TO DISTRIBUTION

FROM Frank J. Wobber

SUBJECT. Revised Planning Document OHER Site-Directed Subsurface Environmental Initiative

Enclosed is a final draft plan for an Office of Health and Environmental Research (OHER) initiative dealing with the subsurface environment. Emphasis in this document, like the previous draft, is on research that is relevant to subsurface contamination, remedial action, and groundwater protection. A strategy for site involvement and suggestions for accelerating the transfer of results to sites are described.

OHER appreciates the guidance that representatives from DOE program offices, DOE Operations Offices and National Laboratories provided during OHER's review workshop on August 6-7, 1987 Many suggestions for improving the document were offered during the workshop and in the comments that we received in the following two weeks. These recommendations were synthesized and incorporated into the plan. If the initiative is funded in FY1989, we will hold additional workshops to obtain suggestions on research priorities and approach.

Please review the revised plan and return any written comments to me by October 9, 1987, limiting your comments to (1) substantive technical errors or omissions, (2) serious problems that affect the accuracy and credibility of the plan, and (3) essential changes or additions to OHER's distribution list.

The final document will be distributed in late October. Your interest and assistance in the proposed program is appreciated.

Frank J. Wobber, Ph.D.
Office of Health and
Environmental Research (ER-75)

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SITE-DIRECTED SUBSURFACE ENVIRONMENTAL INITIATIVE

FIVE YEAR SUMMARY AND PLAN FOR FUNDAMENTAL RESEARCH IN SUBSOILS AND IN GROUNDWATER FY 1989 - FY 1993

September 1987

U.S. Department of Energy
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SITE-DIRECTED SUBSURFACE ENVIRONMENTAL RESEARCH INITIATIVE

Office of Health and Environmental Research
Office of Energy Research

1 0 OVERVIEW

The Department of Energy (DOE) has a strong commitment to lessen the effects of radioactive and mixed waste disposal at sites currently under its control, and to develop more effective waste management practices for the future. The DOE has maintained an ongoing research effort to define and remediate the environmental effects of these wastes. However, the increasing number of waste sites (both DOE and non-DOE) identified nationally for characterization and remediation, in conjunction with spiraling costs, will require major new efforts to understand the nature and behavior of wastes in the near-surface and deep subsurface environment as a basis for developing and evaluating treatment methods. The technical expertise, facilities, and experience of the national laboratory system in dealing with nuclear fuel, fossil fuel, and synfuel cycle wastes can serve as a unique and invaluable base for developing the requisite knowledge to meet research needs.

This initiative, therefore, represents a commitment on the part of the Office of Energy Research to use national laboratory resources and specific university expertise to markedly advance the scientific and technological knowledge required to resolve critical environmental concerns. The mixed nuclear and chemical wastes generated by DOE operations contain chemicals common to wastes from most U.S. industries. Furthermore, the wastes share the potential for contamination of major U S. aquifers. This initiative will, therefore, provide information needed to resolve issues associated with waste disposal at the national level.

The Office of Health and Environmental Research (OHER) has a strong record in basic research that can be applied to site-specific problems. For example, fundamental research on microbial distribution and function in the subsurface, sponsored in part by OHER, is now being used to devise more effective and less expensive in situ treatment strategies for mitigating organic contamination at several DOE sites. Similarly, OHER-sponsored research on radionuclide behavior in soils and natural waters has long been used by DOE sites, other federal agencies, and the international research community to assess effects and establish effective remedial procedures.

The overall goal of this research initiative is to resolve the key technical obstacles to defining and remediating contamination at DOE and other waste sites. To accomplish this goal, the resources of the national laboratories, universities, and DOE sites will be fully utilized to develop and demonstrate improved, cost-effective, and environmentally acceptable techniques for predicting the behavior of contaminants and reducing their concentrations in groundwater The document that follows is a preliminary plan to

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set general research directions for a program extending into the 1990s; detailed plans and priorities will come later.

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2.0 BACKGROUND

The commitment by DOE to clean up inactive waste sites and operate its facilities in a safe and environmentally responsible manner has been demonstrated by Energy Secretary Herrington's elevation of the DOE's Environment, Safety, and Health (ESH) function to an assistant secretary level, and to operate the DOE's inactive waste sites within all hazardous waste regulations The DOE programs needed to meet these commitments require that billions of dollars be spent now and over the next several decades.

Extent of the Problem, Costs, and Current Knowledge

Over the past 40 years, operations by the DOE (and its predecessor agencies) have resulted in the disposal of significant quantities of mixed chemical and radioactive wastes. Paralleling other industries, the DOE is presently in the site discovery and preliminary assessment process. The number, location, and characteristics of these inactive waste sites will be determined for more than 40 DOE facilities across the nation. Even at this early stage of the investigations, several thousand inactive waste disposal sites, tanks, and/or spills containing contaminant mixtures (i.e., mixtures of radionuclides and organic and inorganic compounds) have been discovered.

Realistically, several hundred of these sites will require detailed site characterization to assess the impacts on public health and/or the environment; many will require subsequent remedial action. The cost of monitoring waste disposal operations and characterizing, assessing, and possibly remediating DOE inactive hazardous waste sites will be significant. In testimony to Congress on March 12, 1987, the General Accounting Office suggested that, ". .. *groundwater cleanup can easily amount to hundreds of millions of dollars at a single (DOE) site.*" DOE is presently spending $800 million to $1 billion each year on waste disposal operations.

The resources required to remediate problems at waste sites dwarf those required to characterize and assess the problems. The Superfund Program has shown that the average cost for characterization, assessment, and remedial action design averages $1.7 million per site. At sites much smaller than those found on DOE lands, the remedial action alone averages $12.4 million per site. Typically, 30 to 60 years is required to withdraw and treat groundwater. One facility is currently decontaminating organic material from groundwater; this effort costs $10 million each year and is expected to continue for 30 years.

Technologically, subsurface remediation is in its infancy Scientific understanding of many physical, chemical, and biological aspects of the subsurface is limited by inaccessibility. Delineating the extent of subsurface contamination (which is required before remedial action) currently relies on costly, closely spaced drilling, which may disrupt subsurface flow systems and increase contaminant dissemination These problems have hampered the development of effective remediation techniques

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Mitigating contamination on DOE sites is also complicated by the presence of mixed waste forms for which the long-term chemical behavior and interactions in the environment are unknown.

The OHER Site-Directed Subsurface Environmental Initiative would build upon existing OHER research capabilities. An investment of $150 million over the next five years in the initiative will greatly advance our understanding of the subsurface environment and provide new subsurface characterization, assessment, and remediation strategies to deal with current and future waste management problems in an environmentally sound way. It can provide savings of many times that amount by improving the cost effectiveness of managing DOE wastes. Additional large savings would also be realized by adapting technologies developed under this initiative for use by other federal agency and private sector programs (e.g., Superfund).

Coordination with Other Departmental Activities

Coordination of this initiative with other programs concerned with containing contamination at waste sites and with remedial action programs on DOE lands (e.g., DOE/Defense Programs and DOE/Environmental Health and Safety) will be of the highest priority. OHER will actively seek the cooperation of, and share experiments and results with, all groups concerned with subsurface contamination, remedial action, and waste disposal siting.

Many DOE sites are testing new or improved approaches for treating and disposing of wastes, or accelerating efforts to make basic process modifications that will reduce the volume of wastes being generated. However, below-ground disposal of wastes will not be totally eliminated in the foreseeable future. Thus, the results of this initiative, focused as it is on understanding subsurface systems, will also contribute to improved waste site selection.

Remedial action, site restoration, and site planning are already being conducted at DOE facilities. These sites offer unique opportunities for experimentation and reduced field research costs. For site managers, new information on the transport and fate of contaminants from existing sites will be developed. OHER plans, as part of the initiative, to sponsor seminars and workshops at various DOE sites, to facilitate the transfer of new information to site managers, and to enhance the opportunities for cooperation. However, joint work at field sites that serve both research and site operational interests will provide the most effective mechanism for coordination with, and the transfer of information to, site managers These cooperative field programs will be a measure of the success of the research in addressing critical, site-related problems.

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3.0 RESEARCH PROGRAM

Because groundwater contamination is of pressing concern to both DOE and the nation as a whole, this initiative is focused on the subsurface environment and the factors that influence contamination of this environment. The research is motivated by practical questions at DOE sites (Figure 1). Key questions that need to be resolved include the nature of the waste form, the extent of contamination, and decontamination strategies. These questions are in two categories: those that emphasize an improved understanding of the system, and those that stress mitigation and remedial action based on improved knowledge. The differing information requirements of these two categories have been incorporated into the research strategy.

The research to resolve the questions identified in Figure 1 is outlined in Figure 2. For DOE sites with different wastes, climates, and subsurface environments, controlling processes must be understood at a fundamental level. Emphasis will be on natural processes that control: 1) the mobility and transformation of constituents from DOE mixed wastes; 2) contaminant reactivity, degradation, and mass transport; and 3) the manifestation of these phenomena at the field scale in heterogeneous systems. Fundamental information will then be used to develop new predictive models and sound biological and chemical remediation techniques. These models and techniques will be augmented with more effective techniques to sample contaminants in the subsurface environment. Experimental waste sites provide a way to demonstrate new sampling, measurement, and remediation techniques; observe field-scale processes; and verify models. This research strategy will lead to new techniques and models for waste site characterization, remediation, and management. The following description of proposed research is based on the strategy outlined in Figure 2.

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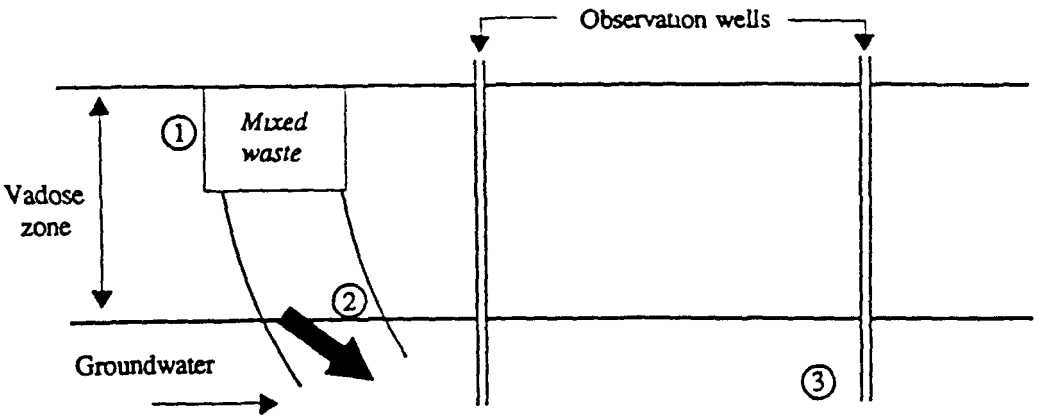

Typical site-specific questions

1 a) What is the nature of the contaminants in the wastes and what factors control their mobilization?

b) How can the contaminant flow to the environment be minimized?

2 a) What is the distribution, concentration, and chemical form of contaminants in the subsurface?

b) Is treatment necessary? How can specific chemicals be removed or destroyed?

3 a) How long will it take and in what form will contaminant mixtures migrate from sources (wastes or subsurface contaminated zones) to uncontaminated areas?

b) How can the migration of specific contaminants be monitored and restricted?

Figure 1. Practical Questions Motivating the Site-Directed Subsurface Environmental Research Initiative

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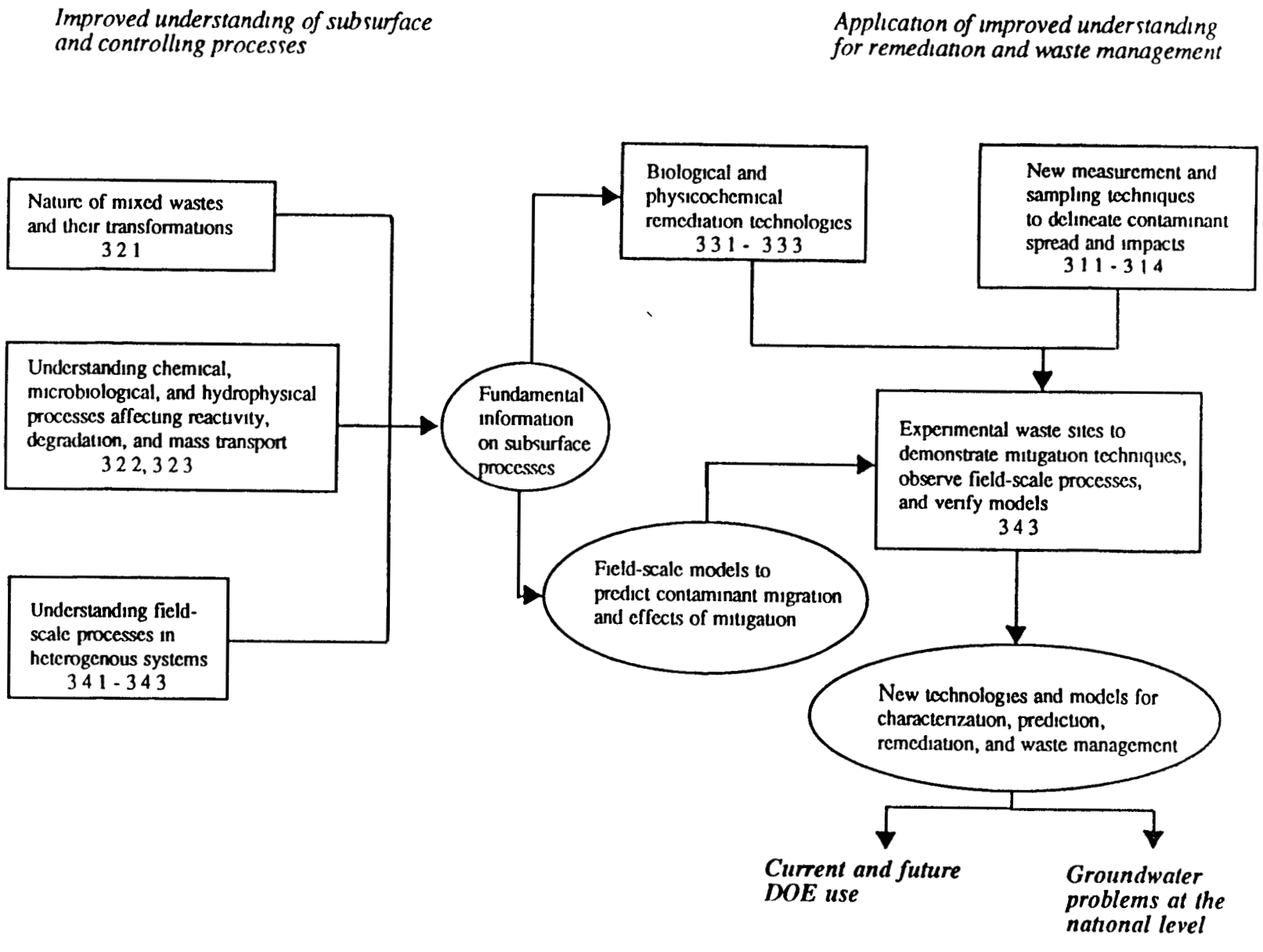

Figure 2. Research Strategy: Site-Directed Subsurface Environmental Research Initiative

approaches for in situ sampling, measurement, and cnaracterization of the near-surface and deep subsurface environments at waste sites.

Collecting and analyzing samples to monitor waste discharges or characterize near-surface and subsurface contamination are extremely costly and time-consuming processes under any circumstances. Additional challenges result from the need to obtain samples that contain sufficient levels of radioactivity and toxic organic chemicals to measure the contaminant form. These problems make new in situ and remote sensing measurement techniques and rapid screening procedures very attractive. The need for better technology can be illustrated by examples of the level of effort currently underway at DOE facilities using existing techniques. For instance, a recent drilling program to develop supplementary subsurface information at one site on a DOE facility cost $2.2 million (this figure could be multiplied hundreds of times if all sites and DOE facilities are considered), and in 1986, one DOE facility performed 25,000 analyses, primarily on samples collected from the near-surface environment. The potential cost and time savings with more advanced technologies are enormous.

Because the chemical and physical characteristics of the near-surface and subsurface environments vary across a site, accurate characterization by separate, widely distributed measurements is limited, at best. For example, at one DOE facility, approximately 1,500 wells have been drilled, tested, and sampled. The installation of the wells alone required an investment of approximately $40 million. However, this aquifer and its contamination are still not fully understood in three dimensions. Installing a large number of wells can also create new pathways for accelerated contaminant movement. The Tuscaloosa aquifer at the Savannah River Plant (SRP) may have become contaminated with trichloroethylene by migration of the material down the side of a faulty well casing. This emphasizes the need for advanced drilling technologies to obtain the most sampling information with the least subsurface impacts. Collecting representative contaminant samples from the vadose zone and aquifers is also a serious technical challenge, requiring advanced statistical approaches to minimize the number of samples and wells necessary, and to maximize the information that can be derived from laboratory and field analyses.

The information and technologies that will be developed from this effort are an integral part of the initiative and will provide the foundation for describing the environmental processes controlling contaminant release and fate (Section 3.2), developing and measuring the effectiveness of remediation and stabilization technologies (Section 3.3), and describing coupled processes and validating models and concepts in heterogeneous systems (Section 3.4).

Through a program of research, it is possible to develop new technologies that will dramatically improve ways in which environmental monitoring and site characterization are presently conducted Research questions to be addressed include:

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- Can in situ sensing technologies that detect specific contaminants at DOE sites be developed?

- Can well-drilling technology be improved to minimize the impacts of drilling and optimize the usefulness and validity of subsurface measurements?

- What innovative procedures and methods can be developed to rapidly and economically screen and analyze contaminants in both laboratory and field samples?

- Can remote sensing technologies and corresponding data integration systems be used effectively to measure the key site and cross-site characteristics controlling contaminant fate?

- Can advanced theory and statistics be used to design cost-effective and representative sampling schemes for the many different types of information required to understand heterogeneous subsurface environments?

- Can a suite of new tracers be developed, or existing tracers be adapted, to perform physical, geochemical, and hydrologic measurements that can reduce the need for detailed characterization and be used to simplify and calibrate contaminant transport models?

3.1.1 Advanced Field Instrumentation and Drilling Technologies

Research Question - *How can drilling and in situ sensing technologies, including extensions of existing technologies (for short-term solutions) and advanced technologies (for long-term solutions), be developed and applied to measuring hydrophysical properties and detecting chemicals, fluids, and their respective tracers?*

Research Description - Chemical contaminants have been released to the environment and detected in the groundwater at waste sites across the nation. Specific examples at DOE facilities include trichloroethylene contamination at Lawrence Livermore National Laboratory (LLNL), carbon tetrachloride contamination at Hanford, and hexavalent chromium contamination at Idaho National Engineering Laboratory (INEL) and Hanford. Noninvasive or in situ measurements to more accurately identify the extent of groundwater and vadose zone contamination would markedly improve site characterization and evaluation remediation technologies. Innovative instrumentation to be developed would include fiber optic chemical sensing devices, such as the recently developed organic chloride optrode at LLNL. Other potentially relevant (but less mature for this application) chemical sensing technologies include direct spectroscopic analysis, surface-enhanced Raman spectroscopy, piezo balance, and surface acoustic wave sensors.

At DOE sites, drilling is the primary method of site characterization and monitoring. Through the drilling process and subsequent monitoring and hydrologic testing, data are collected on geology, geochemistry, water

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quality, subsurface microbiology, and aquifer hydraulic and flow properties It is often necessary to extrapolate from this small window on the subsurface to major areas in three dimensions. Drilling and sampling at most waste facilities are being conducted with techniques that can modify the subsurface environment and obscure controlling chemical microbiological and hydrological phenomena. Thus, research to develop innovative drilling techniques will have immediate benefit to DOE sites.

Acute groundwater contamination problems at DOE sites have occurred from groundwater monitoring wells. This research would also be directed toward methods for grouting or sealing wells. New sealant materials need to be developed that are less expensive, chemically inert, easy to install, provide good bearing capacity, and produce competent bonds between the well casing and the subsurface formation.

Research Objective - The main objective of this research will be to develop and test technologies to accurately access the subsurface environment (through drilling, coring, aquifer sampling, etc.) and measure the location and distribution of contaminants before remediation. Inherent in this objective is the need to advance instrument and measurement technologies to the point where they can be used in conjunction with the advanced predictive and remediation tools being developed in other parts of this initiative. Examples of specialized measurements needed include porous media hydraulic properties, microbial distributions, and the presence of colloidal particles in water. Initial validation of in situ detection technologies will be conducted in intermediate-scale facilities (Section 3.4.1), with the proven technologies applied to field-scale experiments (Section 3.4.2).

Status - Fiber-optics research is underway at most DOE laboratories. A fluorescence optrode developed at LLNL for organic chlorides has already been field tested. A full-scale demonstration at a DOE site is feasible in the near future. Other national laboratories have research underway to develop advanced contaminant concentration, separation, and detection techniques. Conventional techniques for analysis of groundwater grab samples, such as gas chromatography-mass spectrometry (GC/MS), are available at several laboratories for comparison with new methods.

Research efforts addressing chemical species of environmental importance are in various stages of development. For example, researchers at Tufts University have successfully built a portable laser spectrometer for in situ monitoring of naturally fluorescing compounds, such as aromatic hydrocarbons, in groundwater. This may be ready for testing, whereas optrode methods are still under development for copper, cyanide, hydrocarbon fuels, nitrates, phosphate, plutonium, sulfate, and uranium. Sponsoring agencies include DOE, EPA, DOD, and industry. A need exists to develop and test an integrated package of these methods, focusing on specific needs at DOE sites for subsurface characterization and interpretation.

New drilling techniques have been used successfully in hazardous waste site characterization, but taken individually, these techniques have strengths and weaknesses. For example, the hollow stem auger is limited in its

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applicability to shallow environments containing rather uniform unconsolidated sediments State-of-the-science air rotary drilling does not permit the collection of representative geologic samples. However, with careful review, packages can be developed affording the best combination of strengths for specific applications at DOE sites.

Approach - Advanced capabilities will be focused on developing sensors for a range of solutes and solvents in both the laboratory and field. Direct spectroscopic techniques for noninvasive, qualitative analysis using optical fibers and other characterization methods will also be developed. Initial emphasis will be on fluorescence-type optrodes with more conventional techniques, such as GC and GC/MS, used for comparison and standardization. Sensitivity and calibration testing will be conducted with known concentrations and species of relevant contaminants under controlled environmental conditions in an intermediate-scale facility and, ultimately, in the field. Information provided by the DOE environmental audit of field sites, currently in progress, will be used to prioritize sites for instrument field evaluation.

For evaluating well-drilling technologies, researchers with expertise in the pertinent technologies and operations staff with an understanding of the needs of the sites will review current and advanced drilling technologies; the appropriate long- and short-term research and development directions will then be established. Particular emphasis will be placed on developing integrated packages of advanced drilling and sensing technologies to meet site needs in monitoring and interpretation. The new packages would be tested at DOE sites in conjunction with existing site characterization activities. This will allow cost sharing and direct comparison of techniques.

Comments - Several DOE laboratories are on the forefront in the development of in situ chemical sensors and optrode fiber fluorimetric devices for environmental applications. A number of DOE sites and laboratories, engineering firms, and universities have ongoing programs investigating well drilling and development. However, most site characterization activities are driven by immediate regulatory requirements, and there is inadequate attention to the research required to achieve integration of packages and characterization commensurate with long-term site needs (Milestone 1, Table 1). By conducting research and development in conjunction with other efforts in this initiative (characterization, remediation, and validation) and evaluating the new and improved methods at the sites, direct and immediate benefit will be gained by the sites in understanding and predicting subsurface transport processes.

3.1.2 Rapid Screening Methods for Contaminants

Research Question - *Can innovative chemical and biological methods be used in advance of more labor-intensive analyses to rapidly and economically screen and focus efforts on key contaminants in the laboratory and field?*

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Research Description - Traditional analyses of complex, potentially toxic organic and inorganic contaminants, such as carbon tetrachloride, uranium, and mercury, are often technically challenging, extremely labor intensive, and expensive. As such, long time periods between sampling and availability of analytical results may impair key day-to-day waste management decision-making. In many cases at DOE sites, analysis is further complicated by the fact that samples are radioactive. Improved laboratory and field screening methods are needed to provide analyses at the time of sampling, enabling immediate modifications to sampling and analytical protocols during monitoring, field experimentation, and remediation. Simplified chemical detection methods and bioassays based on antibody response or DNA adducts can be used as initial screens for contaminants. Methods might be developed that are less expensive, but still rapid, sensitive, and usable for screening a large number of environmental samples to reduce the number of conventional analyses.

Research Objective - A suite of new screening methods would be developed and adapted for contaminant characterization and remediation investigations at waste sites. The techniques developed should be sufficiently broad and flexible enough to accommodate the range of subsurface contaminant problems to be encountered. Techniques developed should include ways of analyzing samples containing substantial radioactivity because that particular problem is common to most DOE sites.

Chemical and biological screening analyses would focus on 1) surveys for radiological activity; 2) purging methods for volatile organic contaminants in solutions; 3) rapid analyses of solid samples for volatile and semi-volatile organic contaminants; 4) relationships between exposure to contaminants and changes in biological markers; and 5) antibodies and immunoassays for detection of relevant organic contaminants.

Status - The analytical capabilities needed for field screening are at various stages of development. For example, most of the instrumentation required for analyses of volatiles carried out during the recent DOE environmental survey is commercially available. In contrast, field screening for semivolatile organic contaminants will require new analytical methods, such as extraction with supercritical fluid carbon dioxide and direct GC analyses. Preliminary results indicate extraction periods are short (8 minutes or less) and superior to conventional methods, which may take up to 24 hours.

Monoclonal antibodies, developed by industry for use in immunoassays to detect pesticide residues, also have great potential for detecting organic contaminants. In general, immunoassays are very sensitive, specific, economical for use on a large scale, and can be automated. However, they cannot analyze different compounds simultaneously, and a large number of samples are required to justify the development of a monoclonal antibody. Centers of expertise funded by OHER have broad-based experience in biochemical responses of organisms systematically exposed to a variety of contaminants. This experience would provide initial models for research and testing at DOE sites.

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Approach - For radiological screening, the research focus would be on development of small, portable, liquid scintillation counters for total alpha and beta content using thixotropic agents to screen solids. Gamma scanning devices for the laboratory and field should also be developed, preferably using established, commercially available, high-resolution, solid-state detectors.

Analyses of volatile organics in a variety of matrices, including both solids and liquids, can be readily accomplished using commercial instrumentation and documented Environmental Protection Agency (EPA) methods. However, procedures need to be developed for application of those methods in the field to samples with radioactive contaminants and for selective detection of volatiles, such as hexone, that are present in the subsurface at many DOE sites. These procedures and analyses include halogen-selective detectors, electrical conductivity detectors, photoionization detectors, redox chemiluminescence, and mass-selective detection systems.

Analyses of semivolatile organic compounds are particularly challenging. Research would be directed toward measurement of semivolatile organic compounds using new methods of extraction, such as supercritical fluids, which avoid decomposing compounds and mobilizing large amounts of water during analysis. In the latter case, for example, emphasis would be on using the supercritical state (achieved when pressure and temperature are adjusted to remove the distinction between the liquid and gas phases) to permit direct extraction of organics and direct introduction (without any intermediate handling) of the organics into gas chromatographs equipped with innovative detection systems.

In order to effectively use biological markers and immunoassays as indicators of specific contaminants in the environment, a research program is needed to examine biological responses in terms of needed selectivity and sensitivity and to quantitate selected responses for different concentrations and chemical species present in mixed wastes in complex subsurface matrices.

Comments - The DOE laboratories have extensive experience with the development of analytical techniques. These efforts would parallel the development and application of advanced instrumentation (Milestone 1, Table 1), and would be invaluable in implementing the large-scale waste site characterization required by recent legislation.

3.1.3 Quantitative Field, Aerial, and Satellite Remote Sensing

Research Question - *Can remote sensing technologies and corresponding data integration systems be used to provide key measurements critical to contaminant transport and advanced data management and analyses at sites and across sites?*

Research Description - The complex relationships between geophysical-geochemical-biological characteristics in the environment limit our ability

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to predict the fate of contaminants. For example, studies at Oak Ridge National Laboratory (ORNL) have verified that complex geologic bedding and fracture systems have strongly controlled the subsurface movement of disposed waste Accurate three-dimensional measurements of environmental characteristics are required to develop predictive models for assessing contaminant transport and designing remedial action plans. Research is needed to develop methods and software packages for remote detection, integration, and quantification of critical parameters governing contaminant transport, such as geologic structure, geochemical characteristics, soil characteristics, plant species composition, precipitation, evapotranspiration, and hydrogeologic characteristics.

Research Objective - Research will focus on developing 1) the theoretical basis and corresponding methodology to characterize and monitor vital subsurface characteristics that control contaminant movement in a variety of environments, using new remote and ground-based subsurface technologies (e.g., cross-borehole geotomography, three-dimensional high-resolution seismics, imaging spectrometers), and 2) advanced computerized techniques for integration, analysis, and storage of the data sets in three dimensions and at resolutions required for predictive models.

Status - Quantitative remote sensing currently provides regional information on vegetation, soils, and geology efficiently and inexpensively. This capability is critical to understanding the variety of factors that govern transport processes and effects within and between waste sites. Research on advanced remote sensing and near-surface geophysical techniques, including electromagnetic, gravity, magnetic, nuclear, electrical, and seismics, has demonstrated the potential of these systems for providing quantitative, high-resolution, three-dimensional data. Interactive computer systems are now capable of integrating and manipulating large multisource databases These systems will require extensive software development to meet specialized user needs, such as quantitative geologic spatial analysis and the inversion techniques required to define spatial relationships in the geophysical-geochemical-biological data sets.

Approach - The basic approach for developing methods to characterize and monitor contaminant transport and effects on a regional scale rests on advanced remote sensing, geophysical techniques, and data analysis and integration technologies. Initially, remote sensing technologies (satellite, aircraft, ground, and subsurface) and advanced geographical information systems for data storage and integration would be used to identify regional fault planes and fracture systems reflecting crustal stress fields. This information would be projected onto specific sites and used to identify likely conduits for water movement at the intermediate scale. Once these conduits are identified, the main microscale avenues for contaminant movement can be characterized with advanced geophysical methods on the ground. This latter effort will require simultaneous research directed toward seismic, electrical, and nuclear tomography to resolve contaminant flow fields and microstructures (e.g., plant roots) in three dimensions. Databases collected in this manner would be correlated with actual, selected, subsurface measurements to provide models for extension of this information to different sites and regions.

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Comments - Cost-effective evaluation of environmental processes at and between DOE sites will depend on the integration of surface and subsurface data at appropriate spatial scales, generated by new and improved geophysical and remote sensing technologies (Milestone 2, Table 1). The national laboratories have the requisite historic databases that will form the basis for utilization of these quantitative analysis technologies and predictive models for site environmental management.

3.1.4 Advanced Concepts and Statistical Approaches

Research Question - *How can advanced theory and statistics be used to develop optimal environmental sampling and interpretation strategies in order to minimize the number of measurements required and maximize the information available from the data?*

Research Description - Site characterization involves sampling and measuring chemical, biological, geological, and hydrological variables to locate possible contaminants and monitor their dissemination, to identify the processes controlling contaminant migration, and to model the transport and fate of contaminants. The many different types of information required, together with the heterogeneous nature of the subsurface, result in the need for a comprehensive sampling program to provide statistically valid information. However, such programs are extremely costly, and excessive drilling may change contaminant migration. There is a strong need to develop sampling schemes that maximize the information available for the effort invested and maintain the integrity of the natural system. A key to accomplishing this is the development of methodologies to define and obtain samples representative of the most important subsurface characteristics and processes. In addition, the information that results from sampling must be collated, analyzed, and interpreted so that it can be easily used in the field. This will require development and application of innovative approaches for site, cross-site, and trend analyses.

Research Objective - Research will be directed toward development of concepts and methods for optimizing the information derived from a minimum number of properly representative environmental samples, resulting in cost savings and reduced impact on the environment. More accurate sampling information will then be used in conjunction with associated research and monitoring, site characterization, process identification, and model validation.

Status - All methods to optimize sampling require some statistical information before the method is applied. However, at waste sites, the goal is to be able to design an optimum sampling scheme with little or no preliminary data. To date, there has been little progress in this area. Although ad hoc iterative approaches to network design are often employed in practice, there has been little research to develop formal iterative approaches that properly account for the conditional uncertainty in the sampling design.

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The effects of geologic heterogeneities on contaminant migration have been observed at many waste sites. Characterizing these geologic heterogeneities with limited samples is difficult, but innovative methods have potential. One example is an approach to obtain the maximum information about aquifer parameters from aquifer and hydraulic head data based on a combination of parameter estimation and sensitivity analyses. New methods are also under development for interpretation of the information, once developed. These will require further adaptation to unique requirements of the research on this initiative, such as defining the role of microbial populations in contaminant behavior.

Approach - An iterative approach will be developed to determine the optimal sampling scheme for each type of site. This approach will be based on the use of preliminary data to indicate where additional sampling is required.

After preliminary sampling, several sampling designs can traditionally be prescribed, depending on the sampling purpose (e.g., sample clusters followed by regression, stratified sampling, or kriging). However, new methods offer great potential for improving sampling efficiency. For example, when a level of probability can be assigned to the source of contamination and the process by which movement occurs, Bayes strategies (sampling based on prior knowledge) may be employed. In order to select the best method, a suite of increasingly complex subsurface transport scenarios will be developed and tested for efficiency and cost effectiveness using simulation methods. The resulting sampling paradigms will be field tested at waste sites and in cross-site comparisons.

Statistical methods will relate real data sets with contaminant transport models under development as part of this initiative. Success in this effort would result in increased confidence in the models and corresponding decreases in the need for disruptive sampling and analyses.

Comments - Optimizing the environmental sampling and interpretation of field data will result in direct cost savings. In addition, the information can be directly incorporated into efforts leading to the development of predictive models and expert systems (Milestones 3 and 4, Table 1). The national laboratories have the required multidisciplinary expertise (e.g., biologists, chemists, geologists, hydrologists, and statisticians) for such an effort, and have the historic database for testing concepts and demonstrating the value of statistical approaches (Milestone 9, Table 1).

3.1.5 Advanced Tracer Technologies

Research Question - *Can a suite of tracers be developed to perform, at the intermediate and field scales, the physical, geochemical, and hydrologic measurements necessary for establishing fundamental relationships between water and contaminant migration in heterogeneous subsurface environments?*

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Research Description - Chemicals that are either part of the original contamination (tracers of opportunity) or intentionally introduced through a waste stream can be useful in determining the relative direction and rate of groundwater movement, and the fate of chemical and biological constituents within the subsurface environment. For example, the rate of movement of conservative (nonsorbing) and nonconservative (sorbing) tracers may provide integrated estimates of subsurface retention that can be used directly in site-specific subsurface transport models.

Because of regulatory requirements, many tracers are no longer viable options unless they are currently in the groundwater. In addition, tracers of opportunity are restricted to a limited number of facilities and species, making identification of individual sources difficult, if not impossible. Clearly, a tracer must be matched to the particular questions being asked and the hydrologic situation. Because no one tracer will resolve all questions at the many sites being evaluated nationally, new, environmentally acceptable tracers reflecting advanced measurement and predictive capabilities are urgently needed.

Research Objective - Research would be directed toward establishing a suite of conservative and nonconservative tracers that could be used in refinement and calibration of advanced predictive models for heterogeneous situations at waste sites. Initial focus would be on perfluorocarbon compounds, heavy methane, noble gases, and select organic and inorganic ions with the potential to mimic the behavior of key contaminants.

For conservative tracers, principal consideration will be given to development and testing of chemicals to determine the contribution of individual contaminant sources to subsurface aquifer pollution, the extent of dispersion and dilution, the rate and direction of contaminant transport, aquifer hydraulic conductivity, and interaquifer connections. For nonconservative tracers, efforts would be directed toward chemicals that would allow quantification of the rates of specific physical, chemical, and/or geological contaminant removal pathways. Nonconservative tracers would, in conjunction with conservative tracers, provide an average value for the path and duration of contaminant transport in the highly heterogeneous subsurface environment.

Status - Groundwater tracer technology has used many different tracers to study groundwater movement. These have included: yeast, bacteria, viruses, spores, ions (cations and anions), dyes, gases, stable isotopes, and radionuclides. Some tracers no longer added because of regulatory prohibitions include essentially any radionuclide, and radioactive gases, dyes, and freon. Conservative tracers that are still generally usable include bromide, iodide, krypton, and xenon. Tracers of opportunity currently used at some DOE facilities include tritium, uranium, iodine-129, and nitrate. New generation conservative tracers (perfluorocarbons and heavy methane) have been successfully applied in the study of processes involving atmospheric transport and dispersion. These programs in the past have been supported by DOE/OHER at Pacific Northwest Laboratory (PNL), Los Alamos National Laboratory (LANL), and Brookhaven National Laboratory (BNL). Many of the tracer's requirements for atmospheric dispersion studies

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(i.e., nonreactive, nontoxic, low ambient background concentration, and high sensitivity) are similar to those required for groundwater tracer applications. BNL is conducting a detailed evaluation of the applicability of perfluorocarbon tracers in the subsurface environment. ORNL has extensively investigated the use of radiotracers, and Argonne National Laboratory (ANL) has a new program using natural isotopes for tracing and aging. LANL has extensive experience with heavy methane and has developed collection procedures and analytical methods capable of detecting minute quantities with excellent specificity.

A broad range of sensitive instrumentation for detecting inorganic and organic chemicals with the potential for use as tracers (e.g., ICP/MS at PNL and LLNL) is available throughout the national laboratory system.

Approach - Development of a package of chemical tracers for application to site-related problems will require: 1) identification of possible compounds that can be classified as unique tracers (i.e., are absent from or have very low background levels in the environment); 2) performance of physical, geochemical, and hydrologic measurements to determine appropriate constants for preliminary model calculations to assess detection at various distances (dilution effects) from release points; 3) examination of cost-effective ways of obtaining representative samples and measuring concentrations of the tracers in the subsurface environment; 4) performing field testing (as part of the research described in Section 3.4) by controlled releases of tracers in the process streams of active facilities on sites with flow patterns well defined with tracers of opportunity; and 5) recommending a suite of new tracers, in conjunction with new generation contaminant detection and predictive transport models, for use by site managers.

Comments - The DOE is the world leader in tracer technology. Radioactive tracers have been used to monitor the occurrence and dispersion of contaminants from a number of situations. DOE sites provide ideal locations for the development and field testing of organic and inorganic tracer compounds (Milestone 1, Table 1). Information available at the diverse sites could significantly aid in modeling the results from field experiments. Furthermore, this effort would integrate into other large-scale characterization studies [required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), the Clean Water Act, and the Resource Conservation and Recovery Act (RCRA)] currently underway at many of the DOE sites. The technology to measure hydrologic parameters and migration rates of contaminants through an aquifer would thus be compatible with, and directly applicable to, many industrial operations that have released contaminants into groundwater systems.

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3.2 ENVIRONMENTAL PROCESSES CONTROLLING CONTAMINANT RELEASE AND FATE

(.... improved understanding, new concepts, and advanced numerical tools to predict contaminant migration and establish sound remediation techniques)

Predictions of the contaminant flux from waste forms, and of the chemical reaction, biodegradation, and mass transport of contaminants in the subsurface, are crucial to risk and exposure assessment and remedial action Current predictive technology is inadequate to deal with the complex chemical, biological, and hydrophysical interactions that control contaminant form and dissemination because responsible environmental processes are not well understood. Thus, while contaminants on DOE sites have been incorporated into the biosphere through the soil system or have migrated to groundwater, basic research is needed to remediate these impacts and forecast further dissemination of contamination.

As has happened with other industries, past waste management practices at DOE sites have resulted in contamination of groundwaters. Trichloroethylene and tetrachloroethane have been observed in the groundwater at several DOE installations; at another DOE site, carbon tetrachloride was dispersed to the land surface and the ultimate distribution remains to be quantified. Operations at another facility discharged substantial quantities of mercury to the land surface. In addition, radionuclides have been detected in the groundwater at several sites.

Importantly, a lack of predictability seems to characterize the release and migration of contaminants from mixed wastes. Groundwater monitoring at one facility indicated the presence of trichloroethylene, dichloroethylene, and vinyl chloride in a sand aquifer. State-of-the-science solute transport codes that were applied to this site underestimated contaminant movement. Predictions such as these are typically inaccurate, because environmental processes are not understood and are, therefore, incompletely represented in mathematical models. In the preceding example, estimates of contaminant movement were in error because of a lack of attention to sorption mechanisms and contaminant interactions, the extent of microbial anaerobic degradation, and heterogeneity in the physical properties of the aquifer. Clearly, more accurate predictions are possible only after the controlling environmental processes are well understood and fundamental relationships and data are developed to describe their occurrence in the subsurface.

The objective of research in this section is, therefore, to provide a focused understanding of the processes that control mixed waste leaching and contaminant movement and degradation in the subsurface environment. The research will be highly selective, emphasizing processes and pressing scientific questions directly pertinent to waste management and remediation issues at DOE sites. For example, microbiological degradation and chemical sorption and/or complexation in organic-inorganic mixtures, colloid-enhanced transport, and multiphase fluid flow are areas needing significant research The research described in this section will provide DOE sites with more advanced models to forecast the migration of contaminant mixtures, and fundamental information on key processes needed to establish sound remedia-

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tion methods (Section 3.3). These concepts will be further developed and demonstrated in fully heterogeneous complex field sites (Section 3.4).

The ability to predict the migration of contaminant mixtures at DOE sites, and to then establish remediation technologies based on sound scientific principles, can be markedly improved if the following questions are answered:

- What information on long-term chemical reactions is required to predict the release and chemical form of contaminant species in the original wastes?
- Can the combined effects of chemical and biological phenomena that control contaminant reactivity and degradation in the subsurface be sufficiently understood to yield improved predictive models and develop technologies for site remediation?
- What important hydrophysical phenomena influencing contaminant transport at DOE sites are least understood? Can fundamental investigations be performed of these phenomena to improve the theories and predictive models?

3.2.1 Transformations of Mixed Wastes

Research Question - *Can contaminant release from wastes into the environment be understood and predicted from fundamental knowledge of the rates and magnitude of short- and long-term chemical and biologic reactions and transformations in the waste form?*

Research Description - The nature of the waste form controls the identity, rates, and chemical reactivity of contaminants released to the environment. Much of the waste at DOE sites is stored in near-surface waste forms, which are designed to isolate the contaminants from the environment. Examples of isolated waste forms are liquid wastes in large single- and double-shell tanks, liquid wastes in buried drums (low-level waste; e.g., ruthenium, mixed with kerosene at the West Valley, New York site), and liquid wastes sealed in grout that have been buried in the near-subsurface environment (approximately 100 million gallons of low-activity, concentrated nitrate salt liquid waste with low levels of benzene, at SRP)

The chemical nature of the waste (i.e., the identity of solid and dissolved inorganic and organic components) will change with time. Some changes will be short term (i.e., rapid complexation, dissolution, precipitation, or sorption reactions that quickly proceed to equilibrium), while others will be long term, with slow reaction rates. Long-term compositional changes in the wastes may also occur because of temperature changes caused by the heat of hydration or radioactive decay, or because of elemental removal through radioactive decay or leaching into the environment. For example, cobalt-60 was found to preferentially leach out of seepage ponds at ORNL after chelation by EDTA in the liquid source.

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The ability to predict the release of contaminants from the waste source is a critical step in assessing the impact to the environment and designing remediation strategies. Both gas-phase and aqueous-phase emissions can occur. Quantitative prediction of leachate composition and gas-phase effluents is a complicated task that has rarely been accomplished, even for simple waste forms. It requires an understanding of what chemical species exist, what chemical and biological reactions can occur, and valid chemical descriptors of these reactions.

Research Objective - The goal of this subtask is to provide DOE sites with new information needed to assess long-term contaminant release from mixed wastes. This goal will be accomplished through two objectives. First, research will identify the controlling chemical reactions and compile, measure, and validate thermodynamic parameters describing gas-phase, solid-phase, and aqueous-phase equilibria for key constituents common to DOE wastes, stressing the unique characteristics (high electrolytes, immiscible solvents) of these waste forms. The second objective is to develop an understanding of the mechanisms and rates of chemical reactions controlling long-term chemical evolution of the waste form and release of gaseous/aqueous-phase contaminants.

Research in this section will focus on chemical and biological phenomena controlling long-term contaminant identity and release to the environment. Results from this task will provide important guidance on the identity of relevant contaminants and mixtures to tasks investigating contaminant biological/chemical (Section 3.2.2) and hydrophysical (Section 3.2.3) interactions in the subsurface, and mitigation strategies (Sections 3.3.1 and 3.3.2).

Status - Efforts to predict contaminant identity and movement from specific waste forms disposed to the ground at DOE sites have been hampered by the lack of basic thermodynamic data on radionuclide-organic and mixed organic-inorganic compounds, and the magnitude, rates, and products of chemical and biological phenomena that drive long-term change.

Approach - Representative waste form compositions will be identified from site-specific waste inventories that are being developed independently of this initiative. A series of model wastes that span the important waste properties and chemical compositions identified in the inventory will be synthesized for use in experimentation. Dominant short-term, equilibrium chemical reactions (including precipitation/dissolution and liquid/vapor phase changes) that control contaminant release and reactivity in the model wastes will be identified through experimental observations and calculations with geochemical models. Thermodynamic parameters necessary to predict the extent of the major observed reactions will be compiled or determined experimentally. Values for the thermodynamic parameters will be obtained over a range of temperatures that encompass those temperatures experienced by the waste in the field. The applicability of these constants and reaction models to prediction of aqueous concentrations of elements and compounds in contact with the wastes will then be tested through experiments with relevant waste mixtures. Long-term chemical transformations of the waste components, model waste forms, and representative mixed

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wastes will be sequentially investigated to identify important reaction rates and mechanisms, and long-term gaseous, aqueous, and solid-phase transformation products. The rates of these transformations will be quantified, as well as their dependence on waste composition and environmental variables relevant to DOE sites. Emphasis will be placed on the mechanisms, rates, and compositional changes that occur via dissolution/precipitation of inorganic solids, transformations of organic compound and solvent mixtures, valence changes of metals, and organo-metal chelation/association reactions.

Comments - Wastes at DOE sites exhibit different compositions and behavior than industrially derived chemical wastes. Basic research that is focused on DOE wastes and their mixtures is needed to understand the complex reactions and processes that occur prior to release into the environment (Milestone 3, Table 1) and to develop remedial methods (Milestone 5, 9, and 10, Table 1). Expertise in this research area is unique to DOE, having been developed through years of research on disposal of high-level waste forms and solid wastes from advanced fossil fuel technologies. The results of this research will show near-term benefit to site operations by allowing more accurate prediction of the identity and concentration of soluble contaminants released from different wastes and mixtures.

3.2.2 Fundamental Chemical and Biological Processes

Research Question - *Can an understanding of the chemical and biological processes that control contaminant reactivity and degradation in the subsurface be advanced to improve predictions of the environmental behavior of, and devise remedial technologies for, complex contaminant mixtures?*

Research Description - Chemical and biological processes in the subsurface determine the rate of migration of mixed-waste contaminants relative to the groundwater flow. They also control the association of contaminants, their reactivity, and their toxicity to biota. Diverse chemical (sorption, complexation, oxidation/reduction, and precipitation) and microbiological (degradation, oxidation/reduction, uptake, complexation) processes act simultaneously on contaminant mixtures, complicating predictions of both solute transport and the chemical identity and form of constituents originating in the wastes. Unforeseen reactions can significantly influence solute migration in contaminant mixtures. For example, at West Valley, New York, when a mixture of kerosene, ruthenium, and low-level transuranics leaked from buried containers, the kerosene altered the structure of the clays, making them more permeable to fluids. This allowed the ruthenium and associated radioactive materials to seep into an aquifer and, eventually, to nearby wells.

Research Objective - The objective of this task is to provide fundamental information on the dominant chemical and microbially catalyzed reactions that control speciation, subsurface reactivity, persistence, and long-term chemical forms of complex multisolute-inorganic/organic

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contaminant mixtures. Research would focus on contaminant and solute/solvent mixtures of pressing urgency to DOE sites.

Interactions between chemical and biological processes will be emphasized, because these processes occur simultaneously in the subsurface, and the magnitude and nature of one influences the other Furthermore, the chemical environment influences the types and activities of microorganisms. The microbiota, in turn, modify the abiotic reaction chemistry through their metabolic activities. Fundamental theory and data will be provided by this task to develop more accurate predictive models and devise sound mitigation technologies (Section 3.3). Information developed in this section and in Section 3.2.3 (hydrophysical processes) will be linked in Sections 3.4.1 and 3.4.2 to provide an integrated understanding of biological, chemical, and hydrophysical processes governing contaminant speciation and transport.

Status - Relevant information and models of chemical reactions and biological phenomena controlling contaminant fate in the subsurface are under development, but are mostly limited to defining equilibrium distributions of single solute contaminants. In general, these models fail to accurately predict the fate of contaminants in the field environment, even in controlled release experiments where the waste source is known. In part, this failure is due to a lack of understanding of the chemical and biological changes that contaminants undergo following their release to the environment. Circumstantial field and laboratory evidence, such as the West Valley example, demonstrate that complex intercontaminant reactions must be understood to predict migration. Linking hydrologic models with biotic and abiotic reaction chemistry models has not yet been accomplished, yet this modeling capability is critically needed to address complex contaminant issues on DOE sites. The complex nature of surface-solute-organism interactions requires that linked models deal with both equilibrium and time-dependent reactions

Approach - Studies will be undertaken to define important biogeochemical phenomena controlling the interactions between substrata and contaminants and forms of the contaminants. Because all substrata and contaminants cannot be examined, the interactions of well-rationalized, representative inorganic and organic contaminant mixtures with representative surrogate surfaces and substrata will be defined to establish a basic understanding that can be broadly applied. The need for eventual prediction of contaminant behavior in waste mixtures requires that experimental complexity progress sequentially from studies of single and binary contaminant reactions with single mineral surfaces, to more complex studies of multiple contaminant mixtures in contact with mineralogically heterogeneous material. The contaminant mixtures will be chosen based on the inventory of wastes at DOE sites and the findings of work conducted under Section 3.2.1. The rates and equilibrium constants will be determined for important reactions, including complexation/molecular association, sorption of contaminants to organic and inorganic colloids, and heterogeneous nucleation and precipitation. These reactions will be investigated in complex solute mixtures (organic, inorganic) and in the presence of dissolved solvents (miscible and immiscible).

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Studies with pure and mixed microbial cultures from subsurface sediments, near-surface environments, and soil/aquifer materials will probe the transformation rates of organic chemicals in mixtures and solvents, microbially catalyzed metal transformations, and the chelation and accumulation of metals and radionuclides by microorganisms. An integrated chemical-microbial experimental approach is needed to quantify the effects of competing reactions, such as sorption and biodegradation of organic compounds, on the transformation of contaminants.

Comments - This research offers a unique opportunity for OHER to integrate past DOE work on the environmental behavior of radionuclides and organic energy-derived compounds with both ongoing fundamental research on organic chemical behavior in the subsurface, and the ecology and function of subsurface microorganisms, to achieve a knowledge base for predictive models (Milestone 3, Table 1) and remedial measures (Milestone 7, 9, and 10, Table 1).

3.2.3 Fundamental Hydrophysical Processes

Research Question - *Can a fundamental understanding be developed of key hydrophysical processes controlling fluid flow and contaminant transport to accurately predict contaminant dissemination?*

Research Description - Because hydrophysical processes control transport velocities of both the fluid phase and entrained colloids and solutes, they affect the rate and direction of contaminant dispersal in the subsurface environment. They also affect the reaction times available for biological and chemical processes, as well as the sequence with which reactants would be brought into contact with each other in the fluid phase, on dispersed colloids, or on solid surfaces. A prerequisite for predicting field-scale contaminant dispersal is an understanding of fundamental hydrophysical processes occurring in well-defined, homogeneous porous media systems.

Subsurface systems can be conceptualized as containing three types of fluids: the gas phase, the aqueous phase, and organic liquids (if present) that are immiscible with the air or water. Each of these fluid phases is subject to migration. Organic liquids with low aqueous solubilities are often found at DOE waste sites (e.g., TCE at SRP and carbon tetrachloride at Hanford). Because most organic liquids are toxic or hazardous to biota, and some contain dissolved contaminants, the bulk fluid flow of organic liquids is an important mechanism of contaminant migration. The subsurface migration of organic liquids may be a major source of long-term groundwater contamination at DOE waste sites because organic contaminants partition out of the organic liquid into the groundwater that it contacts. Because an associated aqueous or air phase is always present in the subsurface system, prediction of contaminant migration when organic liquids are present requires an understanding of the mechanisms of simultaneous multiphase fluid flow.

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While a variety of hydrophysical phenomena control the dissemination of contaminants within the aqueous (or organic liquid) phase, colloid-enhanced transport and gas-phase diffusion are the least understood. Binding of largely immobile contaminants (e.g., Pu, PCBs) to mobile natural colloids (clays, organic material) in soil solutions and groundwater has enhanced contaminant migration in the subsurface at several DOE sites. Similarly, mobile colloids of contaminant materials can occur in the wastes, because the metallic constituents often precipitate, and these precipitates, along with other natural colloids, are dispersed by the high concentrations of salts which are often present. Diffusion in the gas phase and convective gas-phase movement can be significant components of the migration of volatile contaminants in the vadose zone. Improvements in the current understanding of the mechanisms of these fundamental hydrophysical processes are needed to make sound predictions of contaminant migration.

Research Objective - This task will focus on three poorly understood hydrophysical processes that are important at DOE sites: multiphase organic liquid flow, colloid-enhanced transport, and vapor phase contaminant movement. The objectives of this research are to 1) determine the importance of these processes through direct experimental observation, and 2) elucidate the controlling mechanisms for use in developing new predictive mathematical models. Research will utilize laboratory-scale experiments with homogeneous porous media.

New measurement instruments and methodologies developed in Section 3.1.1 will be needed in this task. Intermediate and field-scale manifestations of the hydrophysical phenomena studied in this task, and their interaction with chemical and microbiological activity, will be studied in other tasks (Sections 3.4.1 to 3.4.3).

Status - The environmental importance of immiscible organic liquid flow and colloid-assisted contaminant transport has been recognized only recently at DOE sites. The basic principles associated with these phenomena are not well understood. Attempts to simulate multiphase flow have indicated the need for fundamental investigations into the physical/chemical interactions between organic liquids and porous media that control permeability and organic liquid retention during wetting and drying events.

Only recently have sites been sampled to ascertain the abundance and nature of organic and inorganic colloids. Very little is known about the natural concentrations, size distributions, and binding affinities of colloids for organic and inorganic contaminants, or about the relationship between fluid flow velocity and colloid mobilization/immobilization and transport. Gas phase diffusion in soil has been extensively studied, but understanding is still limited on the vapor-phase diffusion of contaminants undergoing sorptive and degradative reactions.

Approach - The flow physics of immiscible organic liquids common to DOE wastes will be investigated in saturated and unsaturated systems. Research using organic fluids with viscosities and densities both greater and less than water will establish physical principles applicable to two- and three-fluid-phase systems. The research should progress from

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investigations of static properties (e.g., hydraulic characteristic functions, hysteresis, residual saturation), to investigations of two- and three-phase flow. The theoretical basis for current multiphase flow models will thereby be advanced through experimental observation.

The transport physics of colloids will be investigated in saturated and unsaturated porous media. Inorganic, organic, and biological colloids derived from mixed wastes, or known to be present in the natural environment, will be studied in different electrolyte media with and without reactive dissolved contaminants. Colloid mobilization/immobilization and transport will be studied as a function of colloidal properties known to affect transport, such as particle size distribution and surface charge. Changes in porous media permeability caused by the deposition or removal of colloidal particulates must be investigated to determine the mechanistic dependence on fluid flow velocity and chemistry. Physical factors that govern phenomena, such as pore bypass and volume exclusion, will be quantified.

The gaseous diffusion rates of organic contaminants, alkylated metalloids, and volatiles from organic solvent mixtures will be studied in unsaturated porous media. Relationships will be established among the waste source properties, sorption to media solids, and fundamental physical characteristics of the media. The importance of volatilization from the soil surface should be defined, with emphasis on the proper mathematical representation of the transfer resistance at the soil-atmosphere interface.

Comments - Colloid transport and multiphase, organic liquid flow are contaminant migration processes of major importance at DOE sites. Scientific understanding and numerical models, however, are not available to accurately predict either the role of colloids in transport or the migration of organic liquids in heterogeneous media (Milestone 3, Table 1). This research builds upon the expertise in hydrology at the national laboratories and the universities. Consortia are currently in place to facilitate these interactions.

3.3 BIOLOGICAL AND CHEMICAL REMEDIATION TECHNOLOGIES

(. . for aquifer restoration and long-term management of hydrologic systems at DOE sites)

There are examples of mixed wastes (e.g., tributyl phosphate-tritium at SRP; carbon tetrachloride-uranium-nitrate at Hanford; plutonium-chlorinated organics at INEL; and EDTA-Cobalt 60 at Oak Ridge) at the DOE sites that are not readily treatable with current technology. Because the wastes themselves are quite diverse and the DOE sites are located in diverse geographic regions with extremes in climate, geology, and vegetation, a multi-faceted approach is needed for successful remediation and/or stabilization of contaminated sites. Plant communities influence water infiltration and, therefore, contaminant migration Microorganisms can degrade organic compounds and accumulate, solubilize, reduce, or oxidize metals and radionuclides. Chemical and physical processes can solubilize,

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degrade, or immobilize contaminants. The technology or combination of technologies to be used at a given site will depend on all these factors.

The focal point of this section is on development of select, specialized, remediation technologies However, research in this section will require information from Section 3.1 for monitoring contaminant concentrations and transformations during intermediate-scale and field tests (Section 3.4). Additional information from Section 3.2 will be used to set DOE site and waste research priorities and for a better understanding of the fundamental microbial and chemical reactions for development of specific remediation technologies.

In order to produce effective technologies, research must be targeted at answering the following questions:

- Can integrated soil-plant systems be designed to control movement of contaminants from DOE sites?
- Can microorganisms and microbial processes be manipulated to reclaim or stabilize contaminated soils or aquifers?
- Can innovative, economically feasible, physicochemical technologies be developed to decontaminate soils and water?

3.3.1 Vegetative Remediation Technologies

Research Question - Can integrated soil-plant systems be designed to reduce water infiltration into waste sites?

Research Description - The ability of plants to stabilize soil and transpire water is recognized as a potential advantage in using vegetation in an integrated surface-cover and subsurface-management system. However, less is known of the potential for increasing water loss by changing plant community composition to those species which have low water use efficiencies (i.e., plants that lose water at high rates relative to growth rate). To make full use of this potential, fundamental knowledge must be developed on the combination of soil physicochemical and plant phenologic and metabolic processes that control evapotranspiration of water.

Research Objective - The objectives of this research are to define and quantify the fundamental soil-plant relationships that control water infiltration into waste sites. This information would be incorporated into fundamental models designed to predict water balances as a function of known climatic conditions and native or manipulated soil-plant communities at the waste sites. The research will be closely coordinated with efforts in Section 3.1.3 to quantify these parameters remotely on a regional and site-specific basis.

Status - The DOE system of National Environmental Research Parks (NERP) has provided support and a unified basis for description of soils and plants over most of the major climatic and geographic regions of the

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nation. This information base can now be used to identify major soil-plant systems for study and to place these systems in ecological perspective. Cooperative studies at PNL, LANL, and INEL have examined these systems to establish erositivity and water balance models for arid and semiarid regions and to extend ground-based observations regionally through remote sensing methods. Similar investigations are underway at ORNL on humid regions.

Approach - To develop improved soil-plant cover systems for waste site management, it will be necessary initially to conduct a national survey through the NERP system to identify plant characteristics that can influence water loss under a range of site conditions (humid, temperate, and arid), and to develop competent models to compute the theoretical limits of plant water loss and assess the water-loss characteristics of climax plant species over a range of climatic conditions. This information could then be utilized to simulate water loss for plants under present-day and anticipated long-term climate changes (e.g., elevated CO_2 and precipitation), and in a research program to define the combination of plant morphologic, growth, and vegetation characteristics that allow more rapid water loss and CO_2 exchange. Measurements of the water loss for climax species and plants selected using the above process would be conducted over the range of soil and climate conditions expected at waste sites. Microlysimeters will be useful in assessing actual transpiration rates for each plant species. Measurement of surface energy budgets of plants by spectral radiometry and other techniques will identify changes in plant properties.

These efforts would be integrated with parallel efforts to relate soil physical and chemical properties with plant transpiration of water. This information on the soil-plant system would then be utilized to evaluate integrated plant-soil cover response to climatic variations (i.e., wet and dry cycles), and provide site managers with appropriate tools to assess the effects of, and design soil-plant systems for, minimizing water infiltration while maintaining surface stability. The resulting knowledge of soil-plant water use will be integrated with subsurface hydrologic transport models developed in other tasks.

Comments - The use of integrated plant-cover systems to limit infiltration into waste sites has been investigated by INEL and LANL. LANL has shown that, under semiarid conditions, plant cover density is altered markedly by soil surface features (e.g., gravel admixtures), which changes the microclimate enough to reduce plant stress and increase plant-cover density. PNL is developing deterministic models to predict water relationships as a function of climatic and soil-plant characteristics.

Although transpiration studies are currently being conducted at LANL, PNL, ORNL, and INEL, little, if any, research has been done to quantify the factors controlling the high transpiration capacities needed to reduce infiltration. Normally, the opposite characteristics are sought in USDA and university research, because ideal agronomic plants are those with high water use efficiency; i.e , high carbon gain and low water loss.

Quantifying the role of soil-plant systems in controlling water influx to the sites is critical to achieving Milestone 3, Table 1. Improved methods for reducing infiltration would be demonstrated as part of the efforts outlined in Milestone 8, Table 1

3.3.2 Microbial Remediation Technologies

Research Question - *How can microorganisms and microbial processes be used for in situ remediation of contaminated aquifers?*

Research Description - The extensive ability of microorganisms to metabolize organic compounds and concentrate inorganic ions is recognized as having great potential for the removal of toxicants from the biosphere. Microorganisms also have the ability to adapt to stressed environments, often associated with contaminated sites and, therefore, can function in mixed wastes (e.g., degrade organic contaminants in the presence of radionuclides and heavy metals). Mixed wastes at DOE sites that are potentially treatable using microorganisms include those than have inorganic elements that can be concentrated by microorganisms, or organic compounds that can be sequestered or degraded. However, of the natural phenomena governing the fate of contaminants, biologically mediated reactions and factors limiting biological reactions are the least understood. This is especially true for near-surface and subsurface environments. Effective bioremediation strategies will depend on a thorough knowledge of chemical, physical, and biological factors controlling microbial activity, and the effect of introduced nutrients, electron acceptors, or microorganisms on indigenous subsurface microbial populations.

Research Objective - The ultimate objective of this task is to develop bioremediation and/or stabilization technologies for hazardous wastes. To achieve this goal, research efforts have three phases. First, research will define the microbial communities and activities in contaminated and uncontaminated near-surface and deep subsurface ecosystems at several DOE sites for bioreclamation field testing. Second, innovative approaches will be developed for in situ stimulation of microorganisms indigenous to contaminated sites to degrade contaminants and to act as "biocurtains" (barriers to contaminant migration). Third, researchers will investigate and develop methods for tracking microorganisms introduced into the subsurface, such as adapted or genetically engineered bacteria, and determine the impact from contaminants or the introduction of nutrients on the indigenous microbial populations.

This task would utilize basic information developed in Section 3.2.2 on microbial and chemical degradation and mobilization reactions controlling the fate of contaminants. In addition, technologies developed under this task would be tested at the intermediate- and field-scales, as defined in Sections 3.4.1 and 3.4.2.

Status - Although sewage treatment facilities and the petroleum industry utilize microbial processes for conversion of complex organic compounds, there have been few successful demonstrations of microbial

in situ decontamination of soils or aquifers for contaminants of concern at DOE sites. In situ biological remediation methods have been used to successfully remove approximately 7.5 tons of hydrocarbons from groundwater in West Germany over a 120-day period. While these experiments were conducted on a small scale in a relatively shallow system, they demonstrate the potential of bioremediation for aquifer restoration.

A significant portion of problem organic contaminants at DOE sites (e.g., chlorinated organic solvents) are known to be degraded through microbial pathways. A pilot program at Savannah River Laboratory (SRL) is presently investigating the potential for bioremediation of TCE-contaminated groundwater, using bacteria that can utilize methane or propane as a co-metabolite to mineralize TCE. Persistent contaminants often require co-metabolism or induction of specific enzymes for their degradation. This necessitates maintaining suboptimal growth concentrations of inducers, electron acceptors, and electron and carbon donors, using pulsed delivery systems.

Recent information developed by DOE-OHER on microorganisms in deep subsurface aquifers indicates the presence of diverse communities with the potential for in situ stimulation to accomplish biodegradation, concentration/immobilization, or incorporation into biocurtains to remove or contain energy-related contaminants. Research at PNL has dealt with microbial solubilization and concentration of trace metals. Work underway at INEL utilizes microbial cell components, proteins, and polysaccharides to accumulate specific metals and radionuclides.

Approach - The microbial remediation of contaminants will best be achieved through laboratory, intermediate-scale, and field research focused on identifying the biological, chemical, and physical factors governing microbial metabolism and growth in contaminated subsurface environments. Factors requiring investigation include the characteristics of the organism or a consortia of organisms, the primary substrate and nutrients, the co-metabolic substrates, contaminant concentration, available electron acceptors, and environmental conditions (e.g., pH, salinity, toxicity, radiation, presence of colloids). These factors are interdependent, and research on methods to alter the in situ environment to enhance biological activity must address the combined effects.

The fate of contaminants (such as loss to the atmosphere, mineralization to carbon dioxide, complexation by humics, clays, and microbial cells, or loss into micropores), as well as partial degradation reactions, must be defined

In addition to degradation of organic contaminants, technologies will be developed for using microorganisms to limit the migration of radionuclides or metals, or accumulate them for retrieval. Examples of innovative technologies that research will be directed toward include the reclamation of tributyl phosphate and tritium-mixed waste using microorganisms that degrade the organic moiety and result in phosphate precipitation, the use of phenolic organic compound-degrading microorganisms that complex chromate to treat hazardous waste containing a mixture of these contaminants, and

the use of methylation of mercury by bacteria to produce a volatile species retrievable from the subsurface.

Comments - While hazardous waste is a national concern, mixed (organic, inorganic, and radionuclide) hazardous waste is a problem common to DOE sites. Examples of research in microbial degradation and complexation of contaminants include the isolation of aerobic bacteria from the subsurface at SRL that can mineralize TCE to carbon dioxide and chloride salt, and demonstration by PNL of the degradation of homocyclic and heterocyclic N aromatic compounds by bacteria isolated from subsurface sediments under aerobic and anaerobic conditions.

Field-scale aquifer remediation technology is being developed and tested at SRL to remove TCE from groundwater using bioremediation techniques. Related efforts will be conducted at other sites in the future, including biocurtains to limit subsurface radionuclide migration at INEL (Milestones 7 and 8, Table 1). This technology is an excellent candidate for transfer to the private sector, as TCE and other chlorinated organic solvents are common groundwater contaminants.

3.3.3 Physicochemical Remediation Technologies

Research Question - *Can innovative, economically feasible, physicochemical technologies, such as supercritical fluids, be developed to decontaminate groundwater?*

Research Description - A number of conventional and innovative water treatments are technically viable for the elimination of contaminants (e.g., filtration, ion exchange, air stripping, reverse osmosis, activated charcoal). The main limitation to these technologies is the expense and high energy requirement for removal and treatment of the large volume of materials that are involved. Relatively nonvolatile organics are particularly troublesome in this regard. In situ chemical remediation is generally not feasible with most current technology because of the tendency of chemical methods applied in near-surface and subsurface systems to either make the problem worse (i.e., sulfide addition to precipitate metals), or to replace one problem with another (iron precipitation or clay swelling). There is also the general problem of controlling reaction conditions in the subsurface. However, there are situations where microbial treatments will not adequately decontaminate or stabilize the waste. These situations require development of relatively simple, low energy, high-throughput water and soil treatment technologies.

Two examples of innovative treatments involve fluids in the supercritical state. In one case, supercritical water can be used to readily oxidize organic compounds at relatively low temperatures. Under supercritical conditions, solubility relations reverse, with oils becoming soluble and salts becoming insoluble. In the other case, supercritical carbon dioxide can be used to extract organic compounds for incineration. Under supercritical conditions, carbon dioxide becomes a powerful solvent for many organic compounds. The carbon dioxide conveniently evaporates when

the pressure is released. Both processes can be used to decontaminate substrata and water.

Research Objective - Presently, the fundamental chemistry and physics of supercritical processes are poorly understood and the technology is not well developed. Therefore, the major objective of this work is to understand solubility relationships as a function of temperature and pressure, and to characterize reaction products and dynamics. Research to date has been conducted only on simple, single-component systems. In order to apply this technology to DOE wastes, research will be needed to investigate compound interactions in complex mixtures.

Status - Supercritical water oxidation is currently being pursued at LANL and by several industrial firms. Several pilot demonstrations are planned for FY 1988 and beyond. Supercritical carbon dioxide is used industrially in tertiary petroleum extraction and for decaffeinating coffee. In the laboratory, it is used for chromatography and as a mass spectroscopy sample injection technique.

Approach - Basic research will be performed on the effects of temperature and pressure on the oxidation and extraction of compounds representing the range in chemical and physical properties exhibited by groundwater contaminants at DOE sites. In addition, candidate waste streams, groundwater, and substrata will be tested for the applicability of supercritical reagents to complex mixtures. Based on these findings, larger-scale tests will be designed to address problems of scale, and other supercritical fluids will be considered for applicability to waste treatment.

Comments - Research in physiochemical methods would not be limited to supercritical fluids if other innovative technologies with strong potential can be identified. However, because of the relatively low temperature involved (water 375°C; carbon dioxide 31°C), and because it is not necessary to flash the water to steam in either of these supercritical-fluid processes, they hold the most promise for low-cost, low-energy treatment of organic wastes. Although the supercritical state of fluids has been known for over 100 years, little practical advantage has been taken of the properties of supercritical fluids until the last 10 years. Basic information on contaminant and subsurface properties developed for achieving Milestone 3 (Table 1) will be invaluable. Demonstration of chemical systems would be an integral part of Milestones 8 and 9 (Table 1).

3.4 CHEMICAL, BIOLOGICAL, AND HYDROPHYSICAL PROCESSES IN HETEROGENEOUS SYSTEMS

(.... intermediate-scale and field-scale experimentation for investigating synergistic phenomena and processes manifested in heterogeneous systems, and for validating the instrumentation, predictive models, and remediation strategies to be applied at DOE sites)

The complex heterogeneous nature of the natural environment is a major obstacle to applying specific disciplinary research in basic physical, chemical, and biological processes to the solution of waste site problems. Conversely, without basic research to identify generalized phenomena and mechanisms applicable to other sites, the results of field experimentation are relegated to specific site observations. Investigations of heterogeneous systems to rectify this deficiency are crucial to the development of accurate predictive models and remediation of DOE waste site contamination problems.

Controlled experimental facilities and instrumented waste sites will be developed to allow resolution of key questions related to heterogeneity and scale, but with sufficient control to allow measurement of material balances, and other factors essential to validation of process-level information developed in laboratory studies. In addition, these facilities would be used for demonstration of the advanced instrumentation, sampling design methodologies, and tracer technologies developed in Section 3.1, and the advanced remediation technologies developed in Section 3.3. An improved understanding of processes as they occur in spatially homogeneous systems (Section 3.2) will aid the formulation of hypotheses to be tested in field experiments. The major research questions to be addressed in building an understanding of the complex site contamination problems are:

- What are the interactive effects of simultaneous physical, chemical, and biological processes occurring in subsurface heterogeneous systems where the spatial structure of the heterogeneities is known?

- What techniques must be developed to predict coupled hydrophysical, chemical, and microbiological phenomena in natural systems where heterogeneities in the porous medium properties are variable and uneconomical to characterize?

- What techniques are needed to predict contaminant transport in a natural environment where the source of contamination is complex and its distribution in space and time is not known with certainty?

Several different types of experimental facilities and sites will be needed. Investigations of fundamental processes and comprehensive testing of instrumentation and remediation strategies will require highly controlled, intermediate-scale facilities. Investigations of how to account for the heterogeneities encountered in the natural environment will require selected field sites which are highly characterized as to subsurface geophysical,

biogeochemical, and hydrologic properties. Final demonstration and testing of instruments and remediation technologies, as well as investigations into how to handle complex, uncertain sources of actual wastes, will require instrumentation of actual waste sites. Because of the diversity of DOE sites (e.g., humid/arid, with different major waste components), a number of facilities/sites will be required. Collaboration with, and benefits to, site operations will be highly visible in these field and waste-site-oriented activities. Choices of sites will be made in consultation with site operations and DOE program offices. Milestones 6 to 8 (Table 1) reflect this high site-application potential.

3.4.1 Intermediate-Scale Experimentation

Research Question - *How do chemical, microbial, and hydrophysical processes interact to affect the migration and degradation of contaminant mixtures in heterogeneous systems representative of DOE sites?*

Research Description - Like all natural systems, DOE waste sites and their surrounding subsurface environments exhibit spatial heterogeneities in system properties at the macroscopic scale, such as permeability or reactivity of the porous media. Fundamental information on physical, chemical, and microbiological processes (occurring at macroscopic, microscopic, and molecular scales) is essential but, alone, is not sufficient for predicting contaminant migration in natural systems. It is also necessary to understand the fundamental ways in which system heterogeneities affect contaminant transport. This information cannot be readily developed in the laboratory with one-dimensional flow systems, and may be costly, inefficient, and misleading to accomplish in the field where characterization difficulties may be immense. The interactions of physical, chemical, and biological processes occurring at the mesoscopic (intermediate) scale (where spatial heterogeneity of the porous media system exists) are best investigated in highly controlled facilities where the heterogeneities can be incorporated and examined in an orderly and regulated fashion.

Research Objective - The objective of this task is to investigate individual or coupled processes in systems that exhibit known spatial heterogeneity at the macroscopic scale in some parameter (e.g., porous media properties, microbial population density, fluid fluxes), and that contain multidimensional migration paths. Research will initially be directed toward several key information needs at DOE sites, including· immiscible organic liquids in systems with a water table; the importance of dispersive mass transport to solute movement in layered porous media, or in porous media with heterogeneous inclusions; the evolution of microbial activity and population density as a contaminant plume passes, and the effects of degradation on the contaminant transport; the effectiveness of new remediation technologies or in situ instruments; and the effectiveness of aquifer remediation methodologies that rely on multidimensional injection or pumping.

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Intermediate-scale systems are not intended to duplicate conditions in the natural environment, but rather, are intended to allow controlled investigations of phenomena relevant to the heterogeneous natural environment at DOE sites. The intermediate-scale systems can be intensely instrumented, and they will be used for generation of benchmark data sets to validate contaminant migration models

Quantitative interpretation of intermediate-scale experiments will require an understanding of the chemical, biological, and hydrophysical processes developed in Section 3.2. In addition, the investigations of Section 3.1.1 will provide noninvasive measurement technology that can be employed in the experimental facilities.

Status - There are few investigations of the integrated effects of subsurface chemical, microbiological, and hydrophysical processes in systems with controlled and quantifiable heterogeneity. Artificial aquifer/ lysimeter-type experimental facilities that isolate and highly instrument a volume of porous media have been used in some cases, but the use of "undisturbed" field substrata results in experiments that include the effects of the difficult-to-characterize, complex porous media heterogeneity. Other attempts at intermediate-scale experiments have been hampered by problems with instrumentation and by apparatus designs that mask the phenomena under investigation. Recent advances in measurement technologies indicate that these problems can be avoided.

Approach - Specialized multidimensional experimental facilities will be assembled to study the integrated effects of chemical-biological-hydrophysical processes on contaminant transport. The facilities will incorporate specialized safety features to allow the use of chemical mixtures common to DOE wastes. They will be filled with porous media with known, controlled heterogeneity. State-of-the-science scanning and in situ fiber fluorometric sensing devices will be used to create a dense, spatial measurement network to accurately define contaminant movement and concentrations. The facilities will be used to investigate multiphase fluid flow and the effects of controlled heterogeneity on the chemical and biological processes that affect contaminant reactivity and persistence. An unparalleled opportunity will be provided for proof-of-principle and model validation, as key variables can be controlled and concentration profiles measured with time. Because of the comprehensive nature of the data set collected at each experiment, these data sets could be used as validation benchmarks, thereby reducing the costs associated with validating future advances in theory.

Comments - DOE wastes contain many constituents with undesirable ecological and human health implications. Because of ethical considerations and new environmental regulations, the controlled release of these contaminants to the environment for research purposes is not possible. Controlled facilities and extensive multidisciplinary collaboration are needed to study DOE waste migration under the conditions and scales relevant to the environment. Field studies would parallel the intermediate-scale research. The multidisciplinary collaboration will include laboratory/ university consortia and site operations to ensure a balance of technical

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research and practical applicability. This collaborative use is reflected in Milestones 6, 7, and 8, Table 1.

3.4.2 Field-Scale Experimentation

Research Question - *What techniques must be developed to predict contaminant transport in a natural subsurface system where heterogeneities in the porous medium are spatially variable in a complex fashion?*

Research Description - Field investigations at DOE and other sites have indicated that contaminant migration in natural porous media cannot be exclusively described using only principles developed for migration in homogeneous systems or systems with known, controlled heterogeneity. This is because traditional models require a continuous spatial field, which seldom exists in nature. Yet, specific field studies are extremely costly, and the results often only apply to the specific site under study.

One approach to overcome problems of field heterogeneity is to attempt to find "field-scale-equivalent" values for important descriptive parameters. An alternate conceptualization of the phenomena is that, because of the "random" aspects of the media heterogeneities, field-scale contaminant migration is better described as a stochastic process. Research into natural field-scale processes must begin with experiments utilizing known, controlled waste sources before useful extrapolations of process-level models can be made to sites with complicated disposal histories.

Research Objective - The objectives of this task are to quantify coupled field-scale contaminant migration processes and apply advanced theoretical and statistical concepts to produce predictive models that include rigorous uncertainty analysis. Research will focus on scale-dependent dispersion and chemical retardation, microbiological adaptation/degradation phenomena in the field, and the applicability of various mathematical representations of transport. Models developed in this task will include estimates of prediction uncertainty or confidence interval analysis.

Research in this task will require an understanding of fundamental mechanisms of flow and transport physics, chemistry, and microbiology in homogeneous (Section 3.2.2) and heterogeneous (Section 3.4.1) systems. The work of this task is distinguished from others by the focus on the complications induced by random porous medium heterogeneity as occurs in the natural environment. Field research in this task requires injection of a known waste source, while Section 3.4.3 addresses the complexity of a spatially and temporally distributed waste source that may not be identified with certainty.

Design of the proper sampling scheme will be assisted by Section 3.1.4. The advanced tracer technologies developed in Section 3.1.5 will be essential to characterize the complicated flow and transport patterns induced by the natural heterogeneities.

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Status - Although still incomplete, theories attempting to describe flow and transport in natural media have been advancing. In contrast, validation of these theories in the field and their incorporation into applied contaminant transport models for site evaluation and remediation is only beginning Most work to date has focused on mathematical descriptions of the effects of media heterogeneity on hydrologic properties and nonreactive (i e., tritium, NO_3) solute transport. Little work has addressed the effects of natural field heterogeneity on reactive chemical transport, multiphase flow, colloid transport, or gaseous diffusion. The importance of macropores in natural soils to infiltration and vadose zone transport has been demonstrated by ongoing studies at the Walker Branch field site (ORNL). However, the incorporation of macropore/multiple porosity concepts into applied site evaluation models has barely begun.

Several experimental field sites already exist. For example, at ORNL, two watersheds have been instrumented with a variety of moisture-sensing and sampling devices and subsurface weirs. In addition, ORNL has constructed highly instrumented, soil block facilities to study one-dimensional flow and transport in field soil with natural heterogeneity. Thermal energy storage programs at DOE assisted in the development of a subsurface/aquifer study site near Auburn, Alabama, for studies of vertical permeability and dispersion. Controlled release experiments to study subsurface dispersive and reaction processes have been performed at Borden, Ontario, Canada, with Environmental Protection Agency (EPA) support, and an ambitious subsurface macrodispersion experiment in a heterogeneous aquifer, sponsored by the Electric Power Research Institute (EPRI), is underway in Mississippi. The intent of DOE research, which is planned in cognizance of these past studies, is to investigate the field transport behavior of reactive, mixed-waste surrogates; specifically, the manifestation of linked chemical and microbiological processes in the heterogeneous media. This contrasts with past and ongoing controlled release experiments where the focus is upon the effects of heterogeneity on the hydrologic process.

Approach - Controlled injection or surface application experiments will be performed at a vadose zone field site, at a monitored small watershed with subsurface weirs, and at an intensely-monitored near-surface aquifer. The spatial variability of subsurface hydrogeology, sediments and colloidal particulates, chemical properties, and natural microbial population density will be characterized. Tracer experiments will be conducted first to investigate issues related to subsurface flow and nonreactive solute transport in randomly heterogeneous natural media. Following these experiments will be the injection or application of carefully selected organic and inorganic contaminant mixtures that serve as surrogates for toxic waste forms. The movement, speciation, sorption, degradation, and dispersion of these constituents will be monitored with time.

Details of the injection and monitoring methodology (the experimental design) will be optimized to test specific hypotheses regarding the effect of random heterogeneity on the migration phenomena. These hypotheses will be tested through comparison of experimental results with state-of-the-science field transport theories. Field experiments will also be

designed to act as validation tests for improved water/multiphase flow and multisolute chemical/microbial reaction models. These validation tests will demonstrate whether the responsible subsurface transport and reaction processes have been correctly identified and parameterized in previous research.

Comments - DOE has already developed several experimental field sites near the national laboratories. These sites exhibit physical conditions relevant to mixed waste disposal sites, are well-controlled, are generally free of the immediate effects of residential and commercial development, and have been subjected to geologic and hydrologic characterization. They represent ideal locations for controlled release experiments (Milestones 3 and 8, Table 1).

3.4.3 Experimental Waste Sites on DOE Lands

Research Question - *Can several established DOE waste sites be used to observe long-term waste transformation and subsurface transport processes, test predictive models, evaluate proposed remediation techniques, and facilitate early transfer of research information?*

Research Description - Waste transformations and contaminant migration through vadose and saturated zones are typically slow processes. Often, years pass before contamination from a waste site is observed in nearby waters. Important long-term phenomena controlling migration or transformation of contaminants may occur that might have been ignored or not observed in shorter-term laboratory experiments. It is necessary, therefore, that established waste sites be investigated where long-term phenomena can be observed, substantiated, and compared to predictions from shorter-term experiments and field studies. While such studies may be complicated by a poorly defined waste source, they provide unique opportunities to investigate field-scale questions (e.g., heterogeneity, stochastic processes, microbial adaptation) at complex mixed-waste sites.

It is also important that new generation treatment technologies be demonstrated at representative sites, where complexities in chemical, biological, and physical properties typify other sites.

Research Objective - Carefully selected waste sites on DOE lands will be used in this final task to test and integrate findings, technologies, and models developed in other sections of the initiative. These experimental sites will facilitate coordination both among investigators and between the investigators and the users at DOE sites. The objectives of this task will be to observe the long-term environmental dynamics of mixed wastes and contaminant movement in the subsurface, to investigate how to account for subsurface contamination that has come from numerous sources with uncertain distribution in space and time, and to demonstrate whether controlling biologic, chemical, and hydrologic processes are sufficiently understood, models are accurate, and remediation/measurement/sampling technologies are accurate. The scientific questions that are addressed herein stem from investigations performed in all other sections

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of the initiative. These questions address first, whether the long-term environmental dynamics of contaminant mixtures from DOE mixed wastes conform to predictions derived from smaller scale, shorter-time period experiments (Sections 3.2, 3.4.1, and 3.4.2); second, whether there are important unanticipated processes that influence contaminant behavior in the field (Section 3.2); third, whether new measurement and sampling technologies (Section 3.1) can more accurately delineate contaminant distribution and migration without hastening their dissemination; and fourth, whether newly developed remediation techniques can reduce contaminant concentrations to acceptable levels in a cost-effective manner.

The resolution of these and other questions at the experimental waste sites will ensure that proven technologies, models, and remedial tools are provided to DOE sites at the completion of research in the initiative.

Status - Many hydrochemical characterizations of waste sites have been reported in the literature, including groundwaters impacted with radionuclides (Sr, Co), organic chemicals (wood preserving chemicals, cleaning solvents, aromatic hydrocarbons), metals (Cr), salts, and fossil-energy-derived wastes. These studies have provided insights on geologic, hydrophysical, microbiologic, and chemical processes influencing contaminant distribution. Examples of contaminated sites used for experimental purposes (such as testing specific hypotheses regarding attenuation mechanisms, new remediation technologies or transport model accuracy) are less frequent and are rarely applicable to the complex mixed waste conditions found at DOE sites. The U.S. Geologic Survey (USGS) has used three aquifers containing different contaminant suites as outdoor laboratories to investigate microbial degradation, mass transport, and related phenomena. The Environmental Protection Agency (EPA), in association with Superfund and related activities, has studied in situ bioreclamation at several field sites containing creosote and solvent-derived organic compounds. These past investigations affirm the necessity of verifying the controlling biological, chemical, and hydrologic processes and demonstrating remediation techniques at the field scale. This verification is particularly important under conditions where hydrogeology and hydrochemistry are well understood, and for mixed wastes at DOE sites where many complicated chemical, microbial, and hydrophysical processes simultaneously act upon the waste form and contaminants in the subsurface.

Approach - Research waste sites will be selected at different DOE installations that are representative of DOE mixed-waste sites as a whole. The sites will contain different types of wastes (organic and inorganic) and exhibit different geohydrologic characteristics (vadose and saturated zones). A careful monitoring and sampling strategy will be devised that allows accurate spatial and temporal resolution of the waste composition and properties; contaminant distribution and form in plants, soils, and groundwater; microorganism distribution; and geohydrologic characteristics. State-of-the-science multilevel piezometers, in situ measurement devices in groundwater, and gas-sensing instrumentation on the soil surface will be used to assess changes in contaminant distributions with time. After characterization, the sites will function as ongoing focal points and outdoor laboratories for experiments on monitoring strategies and

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technology, and biological, physical, and chemical remediation and restoration techniques. Predictive models tested in the intermediate scale facility will be further evaluated using data collected from these waste sites and used to assess the success of various treatment technologies.

Comments - The establishment of research waste sites will demonstrate a commitment by DOE to understand and remediate contaminated areas on lands under its jurisdiction. Candidate research waste sites containing relevant contaminants and mixtures are found only at DOE installations or associated lands. These facilities offer an extraordinary opportunity to combine research needs with site operations (Milestone 8, Table 1) and to demonstrate predictive and remediation technologies (Milestones 3, 9, and 10).

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4.0 MAJOR MILESTONES

The results anticipated from this research initiative are summarized below. Assuming full funding of the initiative, OHER expects to demonstrate improved field characterization and monitoring techniques and new laboratory analytical methods within the first two years. Within three years, joint research-site remedial action projects will be established at a minimum of three DOE sites.

Some characteristics of basic research are that it is long term in nature, and that research results commonly transfer through publication in scientific journals. Peer review and publication may add several years to the process. Transfer of results depends on user access to scientific journals or reports, and even if this occurs, technical problems in applying new concepts or techniques develop because the user and the research scientist lack direct communication. Within six months of the start of the initiative, OHER will organize briefings at DOE sites to speed the transfer of results from research already in progress to site managers. To help solve problems with existing mechanisms for research technology transfer, OHER implemented (in 1986) a model program of scientific information transfer and research scientist participation in the remedial action programs at the SRP site.

During the first six to twelve months of this initiative, OHER will extend its successful program at SRP to at least one other site to 1) address existing waste-related problems using new and advanced techniques, and 2) to facilitate interactions between research scientists and site managers so that research advances are rapidly transferred. OHER's experience at SRP shows that this approach has contributed to resolving environmental problems by drawing on the expertise of a diverse, specialized team of research scientists. At SRP, research scientists who otherwise might be unfamiliar with DOE site-specific needs are contributing their expertise to cleaning up contamination within deep aquifers. If traditional research practices had been followed, these scientific skills might have been unavailable for site-specific problem solving. Representative milestones (deliverables) for the FY 1989-1993 period are shown in Table 1.

Priority will be given to refining technologies and new concepts by demonstrating them at selected DOE sites. Joint funding for field demonstrations will be requested from DOE sites, if necessary, once feasibility is established.

The scope and detail of these major milestones may change as additional information on the priorities of DOE sites is obtained, and as the most promising opportunities for technical advances are identified in research proposals received from DOE's national laboratories and others.

Table 1. Schedule for Technology and Information Transfer: Site-Directed Subsurface Environmental Research Initiative

	FY 1989	FY 1990	FY 1991	FY 1992	FY 1993
Improved Site Characterization and Monitoring Technology	*	1	2		
Improved Predictive Technologies	*			3	4
Accelerated Site Restoration and Decontamination - Ecological Methods	*		5 6	7	
Experimental Applications/ Field Scale Demonstrations	*	8		9	10

KEY

* Research Transfer/Joint Testing at DOE sites (see text)

1 Advanced Field and Laboratory Instrumentation
2 Aerial/Satellite Digital Environmental Management System
3 Predictive Models Geochemical-Microbial Organic Chemical Transport Processes
4 Demonstrate Expert Systems - Contaminant Transport
5 Comparative Intersite Information Base - Subsurface Microbiology
6 Biophysical Research Facility Contaminant Transport and Degradation
7 Bioengineering-Detoxification Site Experiments
8 Field Site Interactions Research/Field Experiments Using Current Technologies
9 Laboratory Demonstrations - Mixed Wastes
10 Field Scale Demonstrations - Mixed Wastes

[Legend to Key on next page]

LEGEND - TABLE 1

1 - Advanced Field and Laboratory Instrumentation

This milestone includes prototype packages of new and improved characterization, analytical, and monitoring technologies (with multiplexer for handling multiple measurements), and may also include geohydrological-geophysical packages. The objective is to reduce the number of samples, accelerate data acquisition, provide new information, and reduce costs.

2 - Aerial/Satellite Digital Environmental Management System

Integrated series of remote sensing systems, including high-resolution satellite earth survey systems, for environmental management at DOE sites will be developed. A demonstration (all-digital processing) analysis package will be provided. Aerial/satellite and field survey methods will be integrated.

3 - Predictive Models: Geochemical-Microbial Organic Chemical Transport Processes

Organic chemical contamination is a growing problem at DOE sites. Progress in predicting contaminant transport with consideration of the total subsurface system (sorption/desorption, or retention of contaminants) and microbiological factors or degradation and transport of multiphase fluids will be demonstrated.

4 - Demonstrate Expert Systems - Contaminant Transport

A demonstration expert system to assist in estimating transport of radionuclides and/or other contaminants in the subsurface will be developed. The objective is to provide assistance to site environmental managers in predicting contaminant movement within and outside site boundaries.

5 - Comparative Intersite Information Base - Subsurface Microbiology

An information base to assist DOE sites in decontamination will be developed. A reference set of cultures with information on optimum conditions for degradation will be maintained for use by sites to degrade organic chemical contaminants or to determine the role of subsurface microorganisms in contaminant transport.

6 - Biophysical Research Facility: Contaminant Transport and Degradation

Macrocosms (including one or more intermediate-scale experimental facilities) simulating the basic processes associated with transport and fate of contaminants in the subsurface will be available for use by sites. These research facilities will be housed at various national laboratories and will be available to test alternative decontamination and remedial action alternatives.

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7 - Bioengineering-Detoxification Site Experiments

Using macrocosm facilities, several degradation/detoxification investigations will be conducted cooperatively with the sites These experiments will include new analytical and monitoring techniques developed earlier in the program.

8 - Field Site Interactions: Research/Field Experiments Using Current Technologies

Predictive models and remedial measures will be evaluated iteratively with research and development at DOE sites under different field conditions, and in cooperation with ongoing evaluation and monitoring by the sites.

9 - Laboratory Demonstrations - Mixed Wastes

An experimental series at the laboratory scale to demonstrate the detoxification potential of mixed wastes in situ and with amendments will be initiated. Co-contaminant transport research using prototype intermediate scale facilities will be conducted. Experiments will be modified to demonstrate remedial action techniques as part of a phased program of research through demonstration of new cleanup technologies.

10 - Field Scale Demonstrations - Mixed Wastes

Selected demonstrations of the transport, fate, and effects of contaminants from mixed waste sources will be conducted at several DOE sites in cooperation with site managers.