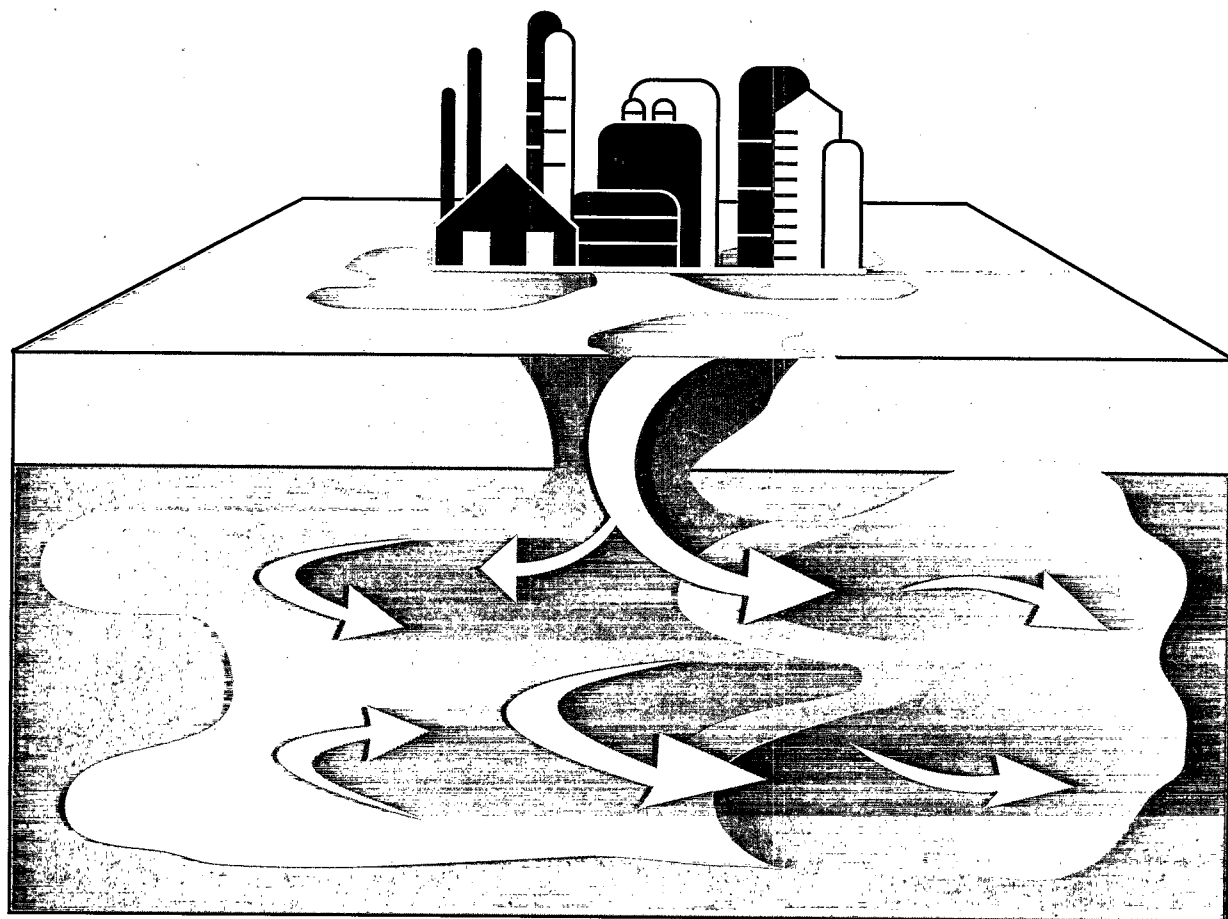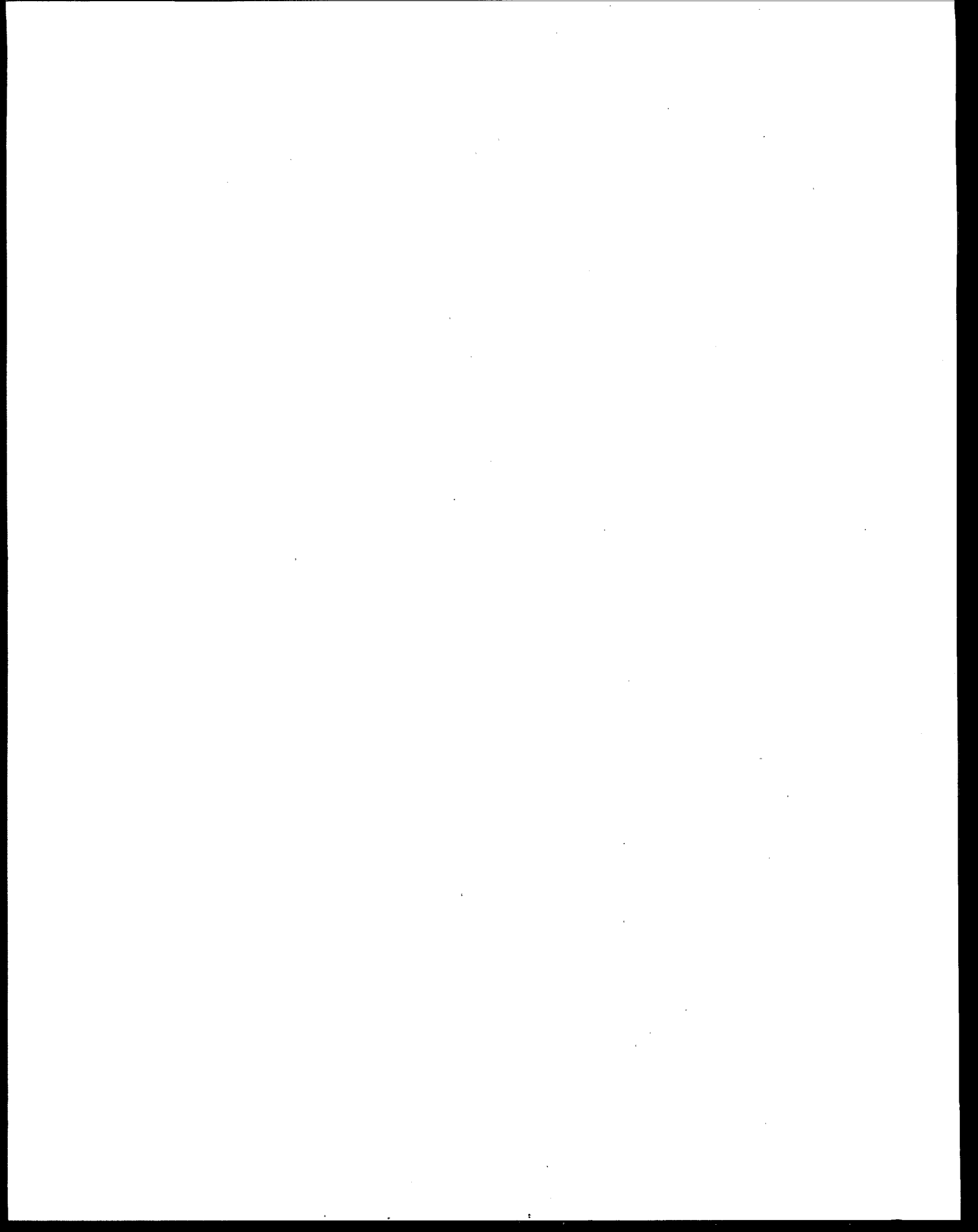**♣EPA**

Abiotic *In Situ* Technologies for Groundwater Remediation Conference

Proceedings

Dallas, TX
August 31 - September 2, 1999

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Notice

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Foreword

The U.S. Environmental Protection Agency (U.S. EPA) is charged by Congress with protecting the nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for reducing risks from threats to human health and the environment. The focus of the laboratory's research program is on methods for the prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites and groundwater; and prevention and control of indoor air pollution. The goal of this research effort is to catalyze development and implementation of innovative, cost-effective environmental technologies; develop scientific and engineering information needed by EPA to support regulatory and policy decisions; and provide technical support and information transfer to ensure effective implementation of environmental regulations and strategies.

This Proceedings document on Abiotic *In-situ* Technologies for Groundwater Remediation is a technical resource guidance document for hydrogeological environmental engineering practitioners.

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Abstract

The U.S. Environmental Protection Agency (EPA) Conference on Abiotic *In Situ* Technologies for Groundwater Remediation was held in Dallas, TX, August 31-September 2, 1999. The goal of the meeting was to disseminate current informaton on abiotic *in situ* groundwater treatment technologies. Although much information is being provided about biotic groundwater remediation approaches, less is known about abiotic processes. There is a recognized need to communicate current design and performance data, technical feasibility, implementation impediments, and cost information to regulators, decision makers, and other stakeholders who would benefit from this type of technology transfer.

The development of cost-effective *in situ* treatment technologies is a major priority for the EPA's Office of Research and Development, the National Risk Management Research Laboratory, and the Technology Information Office of EPA's Office of Solid Waste and Emergency Response. EPA is particularly interested in disseminating information to potential users of these technologies to promote more-effective application to sites that have, historically, been difficult to remediate.

The conference provided information on treatment technologies in the following areas:

- Permeable Reactive Subsurface Barriers (Treatment Walls)
- Thermal Enhancement Treatment
- VOC Stipping Treatment
- Chemical Oxidation Treatment
- Geotechnical Methods and Treatment
- Reactive Zones Treatment
- Technical Practices and Design.Considerations
- Economic Considerations

This document includes conference presentations on these topics, as well as case studies. Presenters are listed on Page 109. These proceedings will be useful to environmental and regulatory personnel at the Federal, State, and local level; university professors, researchers and students; and private-sector personnel including industry representatives and environmental consultants.

Contents

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Acknowledgments

The success of the conference and this document is due largely to the efforts of many individuals. Gratitude goes to each person who was involved.

Presenters and Exhibitors

A special thanks goes to the authors of the papers and demonstrations that were presented at the conference. Their efforts in preparing papers made this document possible and led to the overall success of the conference. The participation of the exhibitors whose displays added to the conference is also appreciated.

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The contributions of the following individuals in the development of the conference are especially appreciated.

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Technical Direction and Coordination

Douglas Grosse, EPA, ORD, NRMRL, Cincinnati, OH, provided technical direction throughout the development of the conference and the preparation of the conference proceedings. Science Applications International Corporation (SAIC) of Reston, VA, handled conference logistics and provided support for many aspects of the conference.

Editorial Review and Document Production

Thomasine Bayless and Jean Dye of EPA's Office of Research and Development, Cincinnati, OH, guided the compilation and editing of this publication. John McCready provided graphics support.
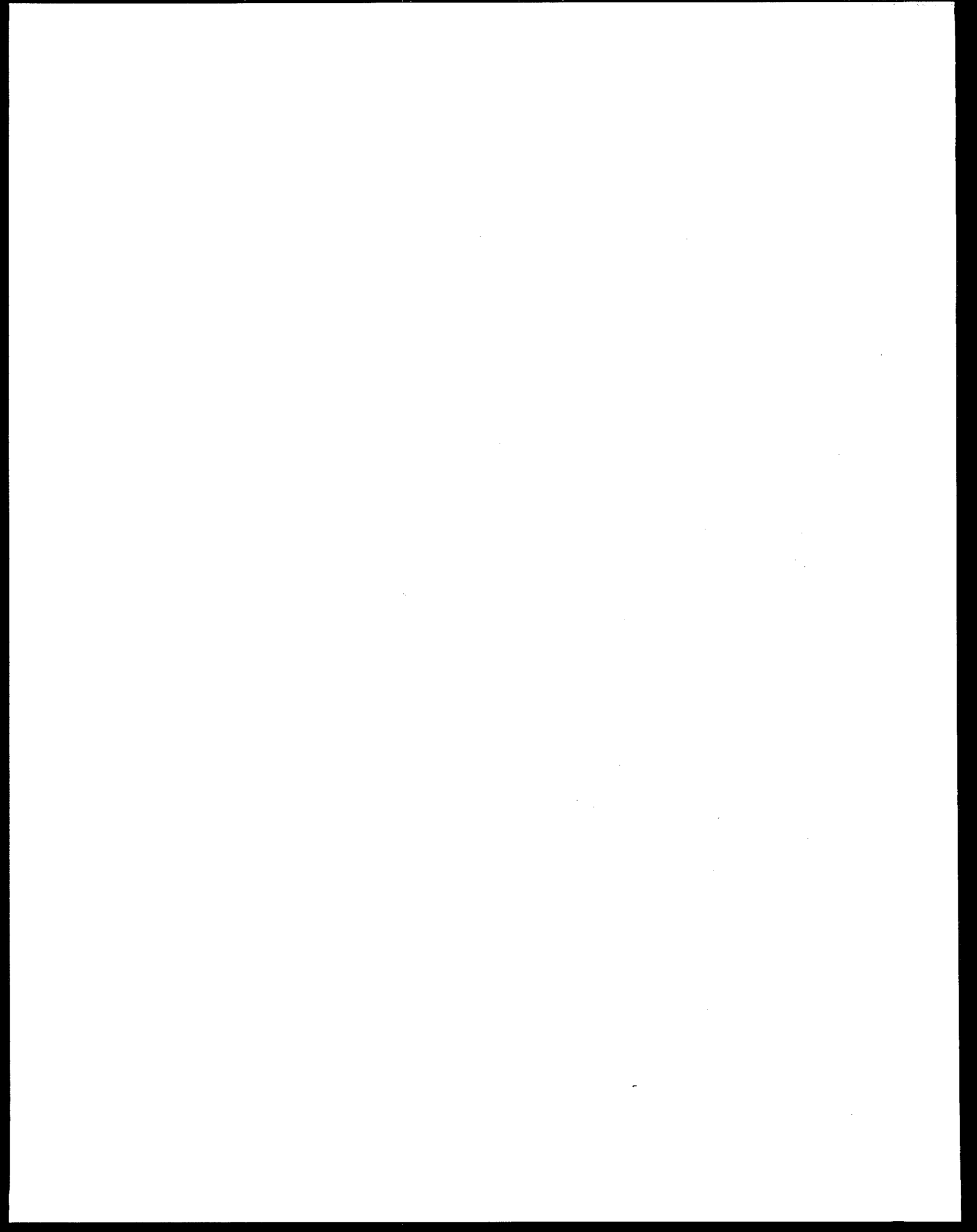
In Situ Abiotic Technologies for Groundwater Cleanup: Current Trends, Needs, and Expectations

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Introduction

The scope of the hazardous waste remediation challenge in the United States is large and diverse in nature. In addition to Superfund sites, corrective action under the Resource Conservation and Recovery Act and leaking underground storage tanks, and clean ups by the Departments of Defense and Energy, emerging state voluntary clean up programs and local Brownfields redevelopment projects offer many challenges. Groundwater contamination is a major issue at many sites; it is further complicated by the presence of nonaqueous phase liquids (NAPLs). Achieving effective and less costly cleanups requires the development and commercialization of improved remediation technologies. *In situ* technologies, in particular, are in great demand because they are usually less expensive and more acceptable than above-ground options. This presentation will summarize important "benchmarking" information for the developers of new groundwater technologies as well as some of the expectations of the user community.

Technology Benchmarking

The USEPA, other Federal agencies, universities, and the private sector have made considerable progress in encouraging the development and use of *in situ* technologies for both soil and groundwater cleanup. Recently, a growing body of information is becoming available about the early application of these new technologies as well as the cost and performance of more established approaches. More than ever it is crucial that new technology researchers be cognizant of the competitive advantages and disadvantages of their new approaches and their relative costs in order to assure the relevance of their work.

Information on *in situ* and other innovative cleanup technologies is available in published reports and electronic databases. Some of the more important information resources are listed below.

The Technology Innovation Office's (TIO's) Clean Up Information (www.clu-in.org or www.epa.gov/tio) web site contains over 300 EPA and non-EPA documents directed at the remediation of soil and groundwater. The listing of other related EPA and non-EPA web sites leads to numerous other sources of such information.

Also sponsored by TIO is EPA REACHIT (REmediation and Characterization Innovative Technologies), the on-line directory of 370 remediation and 160 site characterization technologies along with current deployment information from over 900 Superfund sites. This web-based database, which can searched by media, contaminant, and technology, is located at http://www.epareachit.org.

- EPA has compiled summary information of over 300 field demonstrations of innovative cleanup technologies in North America. Of these 103 are *in situ* soil projects, and 36 involve *in situ* groundwater technologies. The contacts listed in the report can provide more detailed project data. It is available for viewing or downloading at http://www.clu-in.org, and is being updated in 1999. Notable for its major contribution to this body of demonstrations are the over 100 projects for remediation technologies under the EPA SITE (Superfund Innovative Technology Evaluation) program; program-specific information is found at www.epa.gov/ORD/SITE.

- Under the auspices of the Federal Remediation Technologies Roundtable, U.S. federal agencies have prepared a series of 140 detailed remediation case studies, which include some *in situ* technologies (e.g. bioremediation, air sparging, pump and treat, permeable walls). Fewer case studies have been completed on *in situ* groundwater technologies because they have only recently been implemented, and they typically take several years or more to complete. Accessible at http://www.frtr.gov, this web site will include over 200

case studies by the year 2000. In addition, the Roundtable has prepared a guide for gathering cost and performance data that includes several of the newer abiotic technologies. Researchers and others can expect that the parameters outlined in this Guide will be the minimum data sets expected by many Federal users.

- In cooperation with EPA, the Ground-Water Remediation Technologies Analyses Center (GWRTAC) serves as the focal point for information transfer on groundwater treatment technologies. GWRTAC maintains several databases on the development, demonstration, and vendors of groundwater remediation technologies. The Center has also prepared technical reports on 12 *in situ* methods for treating groundwater, including air sparging, bioslurping, electrokinetics, horizontal wells, surfactant/cosolvents, thermal enhancements, and treatment walls. Information is available via the internet at http://www.gwrtac.org.

Challenges for New Technology

Considerable sophistication exists among the consulting and user community about these information resources, so much will be demanded of new technology offerings in terms of their cost and performance data. In addition, the recognition that the problem owner is seeking a total "solution", not a technology, is very important for technology developers. Thus, as in the case of soild remediation solutions with both organic and inorganic contaminants, technology developers will find it necessary to link their ideas together with other technologies to offer the problem owner a "complete" solution. Also, in the area of groundwater cleanup, the invisible nature of the problem and the need to measure the progress of the on-going solution means that *in situ* process monitoring and process control is crucial. Unlike above ground soil remediation technologies, whose operations and results are more easily monitored, *in situ* processes suffer from the lack of robust procedures for problem identification, operational monitoring, and compliance measurement. Thus, new solutions for *in situ* treatment must inevitably be linked with other measurement technologies to guarantee their acceptance.

Beyond these requirements, there are several attributes of previously successful technologies for soil and groundwater remediation that are appropriate for review as developers pursuing new abiotic groundwater solutions. Simplicity, ease of explanation to users and stakeholders, and the "Hippocratic" principle of "doing no harm" are a few of the characteristics that have marked "breakthrough" remediation technologies. It is important to keep these factors in the forefront as developers create new solutions for the difficult world of DNAPL remediation.

Groundwater and *In Situ* Technologies Under Texas Risk Reduction Program Rule

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The purpose of this paper is to explain the groundwater performance requirements of Remedy Standard A and B of the Texas Natural Resource Conservation Commission's (i.e, the Commission's) proposed Texas Risk Reduction Program (i.e., TRRP) rule. The commission is scheduled to meet in Austin on Thursday, September 2, 1999, to consider whether to adopt TRRP as a new chapter in the commission's rules. TRRP will, if adopted, establish a reasonable, consistent, risk-based, performance-oriented process applicable to most waste program areas regulated by the TNRCC with the goals of: appropriately balancing protection of human health and the environment with the economic welfare of the citizens of Texas, and of preserving and restoring the productive use of land. To obtain a copy of the entire rule package, download it from the TNRCC's web site at:

http://www.tnrcc.state.tx.us/waste/trrp.htm

When you download this rule package and start to print it you should be aware that it is over 1000 pages long.

The primary topic of discussion in this paper is the groundwater performance standards under TRRP for each of the two remedy standards with particular emphasis placed on in-situ technologies, such as monitored natural attenuation (MNA). However, in order to provide some context to this discussion of the groundwater performance standards, it is desirable to summarize some general aspects of the TRRP rule as a whole. All of the TNRCC's program areas that will be covered under TRRP, if adopted, include: petroleum storage tanks, municipal solid wastes, underground injection control, voluntary cleanup programs, industrial and hazardous wastes, Superfund, spills, and wastewater treament plants. The primary implementation date is May 1, 2000; however, there is a delayed implementation date for the petroleum storage tank program of September 1, 2003. We started the TRRP project in 1995 when we decided that the two risk-based programs that we had at that time were not consistent and were not working well together. After this we published two lengthy conceptual documents and an ecological guidance document. The agency also proposed and withdrew a draft rule in 1998 and then reproposed this draft rule on March 26 of 1999.

There is a grandfathering of affected properties under the current Risk Reduction Rule. On May 1, 2000, persons shall comply with the requirements of TRRP except as modified by §350.2. Before May 1, 2000, persons may use TRRP once the effective date of the rule has passed. The effective date of the rule is 20 days after the rule is filed with the Texas Register. One aspect of the grandfathering provisions is that a person who has submitted an initial notification prior to May 1, 2000 to conduct a Risk Reduction Standard 1 or 2 response action under the current Risk Reduction Rule and has submitted a final report within five years after that date, may request that the response action be reviewed under the Risk Reduction Rule. Applicants will automatically qualify for this grandfathering if they have received a letter from the agency acknowledging receipt of the initial notification or if they submit other forms of documentation by May 1, 2001 demonstrating that proper and timely notification has been made. Much more detail may be obtained by studying §350.2(m) of TRRP.

Although the entire TRRP process is long and detailed, this paper concentrates on the groundwater resource classification performed during the Affected Property Assessment and on the General Requirements and performance requirements for Remedy Standard A and B.

Determining the classification of the groundwater at an affected property is a key step in the TRRP procedure. The classification of groundwater at a site dictates whether a pollution cleanup or an exposure prevention response approach will be established for contaminated groundwater. The present TNRCC's regulations which classify groundwater include the Risk Reduction Rule classifica-

tion system which represents the approach traditionally taken by the commission to classify groundwater. This approach ascertains whether a groundwater-bearing unit either is a current or potential groundwater supply. Another groundwater classification system used by the petroleum storage tank program is something of an exception since it recognizes four different classifications of groundwater with greater emphasis placed on the current use of the resource and the present location of water wells. The commission has decided to establish an additional class of groundwater (i.e., class 1) due to increased reliance on exposure prevention approaches in the rule and the resulting concern that the most valuable groundwater in the state should be afforded an extra measure of protection by requiring a pollution cleanup approach. The commission has established a separate category for class 1 groundwater to ensure the protection of the most valuable groundwater in the state and to allow some flexibility to take exposure prevention response actions in appropriate circumstances for class 2 groundwater. Adopted criteria for class 2 and class 3 groundwater is essentially equivalent to the definitions for "potential groundwater supply" and "not a potential groundwater supply", respectively.

Determining groundwater classification only applies to a "groundwater-bearing unit" defined as a saturated geologic formation, group of formations, or part of a formation with a hydraulic conductivity equal to or greater than 1×10^{-5} centimeters/second. This means that a saturated clay shale with a dydraulic conductivity less than 1×10^{-5} centimeters/second would not be considered a class 1, 2, or 3 groundwater resource and would not bu subject to the groundwater response objectives. Next, we've been careful to establish that the groundwater-bearing unit must be capable of producing the target yield "at a sustainable rate" (i.e., not a one time occurrence but on a continuing basis) in order to meet a particular resource classification. Moreover, the yield standard for each class is expressed in terms of a groundwater yield for a given size of well; however, a different size well could be used for the test procedure as long as an equivalent yield is used to make the classification determination.

Three key verbs are used within TRRP to define the surface soil, subsurface soil, and groundwater response objectives that must be attained in order to meet the performance requirements for the remedy standards. To "remove" means to take away from the affected property to another location for storage, processing, or disposal. "Decontamination" is a permanent and irreversible treatment process which eliminates chemicals of concern (COCs) at concentrations above the critical protective concentration levels (PCLs). And to "control" is to apply a physical control, such as a cap or a slurry wall, or an institutional control, such as a deed notice or restrictive covenant, which prevents exposure of receptors to COCs.

TRRP is a performance-based rule. By focusing on remedy performance, TRRP should be effective in minimizing technical and regulatory barriers to the deployment of innovative technologies, including in-situ technologies, as long as these technologies can achieve the required performance. For example, to attain Remedy Standard A, the person must, within a reasonable time frame given the particular circumstances of an affected property, remove and/or decontaminate the surface soil, subsurface soil, and groundwater protective concentration level exceedence (PCLE) zones, other environmental media, hazardous and non-hazardous waste to achieve COC concentration levels below the residential or commercial/industrial critical PCLs, as appropriate. Remedial alternatives, including the use of MNA as a decontamination remedy, must be capable of achieving the Remedy Standard A objectives within a reasonable time frame, given the particular circumstances at the affected property, and must be appropriate considering the hydrogeologic characteristics of the affected property, COC characteristics and the potential for unprotective exposure conditions to continue or during the remedial period. Note that MNA, as well as any other in-situ technology, must qualify as a decontamination action, rather than a control measure, to be used under Remedy Standard A. In other words, natural attenuation based upon biodegradation would be an acceptable remedy under Remedy Standard A, while natural attenuation based upon adsorption, which is non-permanent and reversible, would not.

The commission does not plan to specify across-the-board what is a reasonable time period for the completion of response actions at all affected properties in Texas. This rule is to be applied on a site-specific basis where the individual program area is compared against the required performance to establish remedial time frames. Likewise, the commission is not specifying the details for the numerous groundwater response methods which could be used, but rather is defining the performance that whatever method is used would have to attain. Evaluation by the commission of the reasonableness of the use of MNA, or of any in-situ technology, will be based on data contained in the self-implementation notice (SIN) and the response action effectiveness reports (RAERs). The RAERs are to be submitted at least every three years to document whether sufficient progress is being made to achieve the remedy. If a person can demonstrate that an in-situ technology will achieve the response objectives within a reasonable time frame, the technology would be an acceptable remedy. The agency is prepared to reject soil and groundwater response plans when it is clear from the beginning that they will not work or will work so slowly that the response time cannot be considered "reasonable". The executive director may require a demonstration of the appropriateness of the remedy. If the executive director determines either that insufficient progress is being made toward attainment of the remedy standard or that the response action is inappropriate, then the executive director shall require the person to perform an alternative response action. Finally, the provision expressed at §350.31(h) allows the executive director to require an institutional control to be recorded if a response action is

either predicted to take or does take in excess of 15 years to be completed. This process is designed to encourage the early completion of response actions.

In summary, Remedy Standard A requires the use of pollution cleanup, walk away response actions. COCs must be removed and/or decontaminated to the critical PCLs throughout the soil, groundwater, and other environmental media at an affected property within a reasonable time period. No physical controls, such as a cap, may be used. While attaining the groundwater response objectives, the groundwater PCLE zone is not allowed to expand. Under Remedy Standard A, the presence of non-aqueous phase liquids (NAPLs) or a demonstration of technical impracticability cannot be used to justify variance from the basic requirement to reduce the COC concentrations in all environmental media to at or below the critical PCLs. Remedy Standard A is a self-implementing standard which means that once a person files a SIN with the commission, the person may perform the response action without receiving written approval. Since physical controls are not allowed, there is no need for either post-response action care or financial assurance to perform post-response action care. And finally, there is no institutional control required for residential land use under Remedy Standard A. However, an institutional control is required for commercial/industrial land use.

To achieve Remedy Standard B, the person must remove, decontaminate, and/or control the surface soil, subsurface soil, and groundwater PCLE zones, other environmental media, hazardous and non-hazardous waste such that human and ecological receptors will not be exposed to COCs in excess of the critical PCLs at the prescribed, or any approved alternate, points of exposure (POEs). Since physical control measures are typically used to achieve Remedy Standard B, such response actions are generally referred to as "exposure prevention" remedies. As with Remedy Standard A, the person must demonstrate that the response action will be completed within a reasonable time period. There is, however, a substantial difference between the performance requirements for the two remedy standards. For Remedy Standard A, a COCs concentration must be reduced to the critical PCL throughout the soil and groundwater PCLE zones. The performance for Remedy Standard B is more achievable. The soil and groundwater PCLE zones must be removed, decontaminated, and/or controlled such that the critical PCLs are not exceeded at the POEs. In other words, the concentration of COCs does not necessarily need to be reduced to the critical PCLs throughout the PCLE zones so long as human and ecological receptors will be prevented by physical controls from being exposed to this material at the prescribed or approved alternate POEs over the long term.

Under Remedy Standard B, with one exception, a person may use a remedy which involves removal and/or decontamination, removal and/or decontamination with controls, or controls only. That exception is PCLE zones in class 1 groundwater which must be removed and/or decontami-

nated to the critical groundwater PCL for each COC. The person is restricted to a pollution cleanup response action because the objective is to restore the class 1 groundwater to its beneficial use. Thus, the required performance is to reduce the COC concentrations so that they are below the critical PCLs and not merely to contain and prevent the groundwater PCLE zone from spreading. Also, the TRRP rule takes a pollution prevention approach for any class 1, 2, or 3 groundwater-bearing unit which does not contain COCs above the critical PCLs. In further contrast to Remedy Standard A, MNA or other in-situ technology, whether it is a decontamination or physical control process, could be used under Remedy Standard B, provided it is capable of attaining the groundwater performance objectives.

Remedy Standard B is not self-implementing. A person must receive the executive director's written approval of an affected property assessment report (APAR) and response action plan (RAP) before commencing the response action. Institutional controls (i.e., deed notices, restrictive covenants, and equivalent zoning or governmental ordinances) are required more extensively under Remedy Standard B than A. Institutional controls are required for either residential or commercial/industrial land use, whenever the response action takes in excess of 15 years to complete, whenever a physical control is used, whenever a modified groundwater response approach is used (i.e., waste control unit, technical impracticability, or plume management zone). Whenever physical control measures are used to address the soil and/or groundwater PCLE zone(s), the person must perform the post-response action specified in the approved RAP. Also, whenever a physical control measure(s) is used, the person must provide financial assurance adequate to perform the post-response action care.

The general groundwater response objectives for Remedy Standard B are expressed at §350.33(f)(1). Unless one of the modified groundwater response approaches described in (f)(2), (f)(3), or (f)(4) is approved for an affected property, these objectives apply to class 1, 2, and 3 groundwater. The person must use either an active restoration approach or MNA (or an in-situ technology) to reduce the concentration of COCs to the critical PCLs throughout the groundwater PCLE zone. The person must also prevent expansion of the groundwater PCLE zone, prevent migration of COCs to air or surface water above the PCLs, and prevent human and ecological receptor exposure to the groundwater PCLE zone.

§350.33(f)(2), pertaining to waste control units, excludes the groundwater throughout that portion of the groundwater PCLE zone directly underlying a waste control unit from the requirement to meet the groundwater restoration requirements. Beyond the perimeter of the waste control unit, the response objectives must be met. In response to §350.33(f)(3), a technical impracticability demonstration can be used for all three classes of groundwater. The person must demonstrate that it is not feasible from a physi-

cal perspective using currently available technologies to reduce the concentration of COCs throughout all or a portion of the groundwater PCLE zone to the critical PCLs within a reasonable time frame. Where possible, the person must reduce the concentration of COCs to the critical PCLs for any portion of the groundwater PCLE zone where it is technically practicable. The person must prevent migration of COCs from that portion of the groundwater PCLE zone which satisfies the technical impracticability demonstration. Also, the person must prevent COCs at concentrations above the critical groundwater PCLs from spreading beyond the existing boundary of the groundwater PCLE zone. The person must also satisfy the requirements for NAPLs which are expressed at §350.33(f)(4)(E) in the rule and summarized later in this paper.

Plume management zones (PMZs), the final modified groundwater response approach, are discussed in substantial detail in §350.33(f)(4). A PMZ may be established under Remedy Standard B only for PCLE zones in class 2 or 3 groundwater, not class 1 groundwater. The key to a PMZ is, if approved, the POE to groundwater will be changed from throughout the groundwater PCLE zone to an alternate location situated some distance hydraulically downgradient of the existing PCLE zone. This alternate groundwater POE is established in accordance with §350.37(l) or (m) for class 2 or 3 groundwater, respectively. Approval of a PMZ by the executive director is not automatic. §350.33(f)(4)(A)(i) and (ii) present a substantial list of groundwater and surface water factors which are to be considered to determine whether such an approval would be appropriate.

This paragraph looks in a general manner at the establishment of a PMZ in class 2 groundwater. Not all pertinent details are discussed. The analysis starts with a determination of the current length of the residential groundwater PCLE zone as of the submittal date of the RAP. The length of the PMZ is equal to the length of the residential PCLE zone plus a distance "x". The objective is to determine the distance "x" since that is the acceptable distance that a PCLE zone could expand. The maximum additional length (i.e., x) of the PMZ is established as the smallest of the following applicable distances: (1) up to 500 feet beyond the current length of the residential-based groundwater PCLE zone; (2) a length of up to 0.25 times the current length of the residential-based groundwater PCLE zone (i.e., up to 25% additional plume length); (3) to within two years groundwater travel time of the closest hydraulically downgradient off-site property (a) for which the owner has not provided written concurrence to allow the recording of an institutional control or (b) which does not contain the residential-based PCLE zone and the groundwater has a reasonably anticipated future beneficial use; (4) the current extent of the residential PCLE zone when the residential groundwater PCLE zone is already within the two-year travel time setback distance; or (5) the distance to a surface water POE. As an exception, when the affected property is subject to zoning or a governmental ordinance which is equivalent to the deed notice, voluntary cleanup program certificate of completion, or restrictive covenant which would have otherwise been required, the criteria of paragraphs (3) and (4) do not apply.

The final subject of this paper is to summarize how NAPLs within PMZs must be managed. This also applies to NAPLs within technical impracticability zones. The wording of this requirement has been modified and no longer requires that "NAPLs be removed to the maximum extent practicable". Instead, TRRP requires that a person reduce NAPLs which contain COCs in excess of PCLs "to the extent practicable". First, the agency is not requiring NAPLs to be removed solely because they are in a free phase form. The NAPL must contain COCs in excess of the PCLs to be of concern. Second, the rule establishes the following criteria which the person and the executive director will use to determine the required extent of NAPL removal: whether readily recoverable NAPLs have been recovered; whether the NAPLs will generate explosive conditions; whether the NAPLs will discharge to the ground surface, to surface waters, to structures, or to other groundwater-bearing units; whether there will be increased NAPL extent; and whether critical PCLs will be exceeded at POEs. The extent of NAPL removal efforts to satisfy the "to the extent practicable" requirement will be determined on a case-by-case basis depending upon the circumstances at the particular affected property.

Persons who are interested in obtaining future guidance pertaining to TRRP should periodically check the TNRCC web site cited in the first paragraph of this paper for new material. The agency plans a significant effort to prepare guidance to explain TRRP and to facilitate its implementation.

Overview of Abiotic Subsurface Remediation

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The poor performance of pump-and-treat systems in the early to mid 1980s provided an impetus for research to better understand abiotic subsurface processes and to apply the results of that research to the development of better aquifer remediation technologies. Subsurface heterogeneity, sorption of contaminants to aquifer solids, and the presence of nonaqueous phase liquids (NAPLs) were recognized as significant barriers to successful aquifer remediation. In addition, inadequate site characterization severely limited the probability of success. Research on subsurface processes led to the development of new remediation technologies, based on applications of subsurface *in situ* abiotic processes, to overcome the factors limiting remediation success. Many of these new technologies have proved successful in small-scale field tests, but only a few have been evaluated at full field scale, and even fewer are in common use. The next few years are likely to prove crucial in bringing the results of this research to fruition and moving these technologies to regular use for site cleanup.

Introduction

Aquifer remediation was begun in earnest in the early to mid 1980s, largely in response to the new Superfund legislation which required the restoration of groundwater quality at NPL sites. Early efforts relied almost exclusively on what came to be known as "pump-and-treat." Pump-and-treat was based on the idea that the contaminated groundwater could be extracted from the aquifer, treated, and either returned to the aquifer, or otherwise disposed of, while the extracted water was replaced by clean water. Most of these early systems were designed using practices that had proved successful in the development of ground-water supplies for public, agricultural, or industrial use, but were not optimized for aquifer cleanup. A study of 19 pump-and-treat systems by the EPA's Office of Emergency and Remedial Response (OERR) in 1989 concluded that while many of these systems had achieved mass removal and some degree of plume control as well as reductions in contaminant concentrations, most of them were not achieving aquifer restoration and would not be likely to do so at any time in the foreseeable future. The causes of poor performance for the systems in the study included subsurface heterogeneity, sorption of contaminants to aquifer solids, the presence of NAPLs, inadequate site characterization, and poor system design. Among other results of this study was a realization that new approaches for aquifer remediation were needed and that this required a major research effort.

Solving the Problem

As a result of the widespread recognition of the problems of these early pump-and-treat systems, research was initiated by the EPA and other federal agencies, along with the academic community and other organizations, to better understand subsurface contaminant transport and fate processes and to apply that understanding to develop and evaluate innovative subsurface remediation technologies. Many of these innovative technologies are the subject of this conference and are based on application or manipulation of abiotic subsurface processes. There has also been research to develop better subsurface contaminant transport and fate models that integrate process-level models and may be used to design and evaluate these new remediation technologies. At the same time there has been a parallel research effort to develop better subsurface site-characterization technologies.

All of the abiotic *in situ* technologies that we will hear about at this conference rely on one or a combination of two basic approaches. They either apply subsurface abiotic processes to transform or destroy the contaminants *in situ* or use abiotic processes to enhance contaminant removal for subsequent surface treatment or disposal. A wide variety of approaches have been developed to accomplish both of these objectives. While recognizing that subsurface contaminant problems need to be addressed as a whole, including the vadose zone, the source area, and the dissolved plume, it is often fruitful to apply different approaches to different portions of the problem. For ex-

ample, dealing with the dissolved plume initially may be sufficient to limit or control risk to down-gradient receptors while allowing time to develop a remedy for the contaminant source. Permeable reactive barriers often function in this mode.

Most of the technologies that we will hear about at this conference are designed in one way or another to overcome the barriers to aquifer cleanup that were identified by the OERR study: aquifer heterogeneity, sorption, and the presence of NAPLs. They are also looking to do so in the most cost-effective manner.

As a consequence of subsurface heterogeneity, contaminants are often sequestered in low permeability zones that are interspersed among zones of higher permeability. Movement of the contaminants out of these low permeability zones is often limited by diffusion rates which tend to be slow relative to advective transport. There is no way to completely overcome this problem, but a variety of approaches can lessen its impact. Abiotic technologies that address this problem include the addition of energy to heat the aquifer using steam, hot water, electrical resistance heating, or radio-frequency heating. Electrokinetics is another alternative for dealing with zones of low hydraulic conductivity. Permeable reactive barriers can be a cost-effective way around this problem if the goal is protection of down-gradient receptors. In addition, better system design, including the use of wells that induce vertical flow also address this problem. Heterogeneity is one of the most prominent features of fractured rock sites which, to date, remain a major challenge for successful subsurface remediation.

Sorption of contaminants to aquifer solids reduces the rate at which they can be removed by extraction technologies. Technologies which address the issue of sorption include the addition of thermal or electrical energy to increase the rate of desorption or the addition of a chemical agent that will increase contaminant solubility and effectively change the partition coefficient. Addition of a chemical reactant, such as an oxidant, may also be used to destroy the sorbed contaminant. Conversely, particularly for inorganic contaminants, sorption may provide a means of sequestering the contaminant so that its concentration in the adjacent groundwater is reduced. Some permeable reactive barriers are examples of this approach.

The presence of NAPLs presents some of the most challenging problems for subsurface remediation. Most abiotic technologies that address this problem try to increase the rate at which the contaminant can be removed by increasing its solubility or its mobility through the addition of a chemical agent, such as a surfactant, or a physical agent, such as heat. Thursday morning's session on *in situ* flushing will provide an extensive review of the status of efforts to remove NAPLs by increasing solubility or mobility.

The Current Situation

Abiotic *in situ* subsurface remediation technologies appear to be at a critical stage in their development and implementation. Pump-and-treat is now better understood, both in terms of what it can reasonably be expected to accomplish and how to design systems that operate more effectively, and pump-and-treat is still the single most commonly used ground-water remediation technology. Innovative technologies that will be discussed at this meeting are making progress, although most have yet to be widely used for site cleanup. Included among those in more widespread use are air sparging combined with soil vacuum extraction, permeable reactive barriers, and to some extent, thermal technologies. In addition, monitored natural attenuation, which, for organic compounds, relies predominantly on biodegradative processes, is being implemented at a number of sites, usually in combination with some other remedial technology. Other technologies are still at some sort of demonstration/evaluation stage ranging from field pilot scale to full scale. Included in this group are *in situ* flushing, *in situ* oxidation/reduction, and the use of reactive zones.

Current Needs and Issues

While a great deal of progress has been made in the last ten years, there are still a number of needs and issues that need to be addressed before abiotic *in situ* remediation technologies will fulfill their promise. In addition to technology-specific needs, there are also general issues that cut across most of the technologies that will be presented and discussed at this meeting. For those technologies that have shown success in field pilot-scale demonstrations, a critical next step is to take the technology to a larger scale demonstration and to get it in use for an actual site cleanup. For those technologies that have been implemented at one or a few sites, the next goal is to make the leap to becoming accepted practice for site remediation. An important part of this transition is the acquisition of credible cost data and the development and evaluation of cost models that can be used for system design.

No technology is likely to remove 100 percent of the contaminants that are present at a site. Consequently, it is important to determine the benefits of partial mass removal. Another way to phrase this issue would be in terms of relating mass removal to risk reduction. This is an active area of research, but the questions are far from resolved.

Better site characterization, while not the subject of this conference, is a continuing need and intimately connected with the success of all subsurface remediation technologies. This need is particularly great for sites with complex hydrogeology, including fractured rock. Site characterization is closely related to the problem of actually measuring the performance of a subsurface remediation technol-

ogy. In many situations, the reported performance of a technology may be highly dependent on how it is measured. Needs in this area include both specific measurement techniques and more general agreement on benchmarks for measuring performance. There is a need for both pre- and post-cleanup monitoring methods and real-time methods to measure the ongoing progress of a remedial action.

Many sites will require different approaches for different parts of the site. As a result, there is a need to better understand how to link technologies together to achieve site cleanup in the most cost-effective manner.

One conclusion to be drawn from this brief overview is that, while a great deal of progress has been made in improving the effectiveness of subsurface remediation technologies, there is still a great deal of work yet to be done before the promise of innovative approaches is realized.

Disclaimer

This is an extended abstract of the proposed presentation. It does not necessarily reflect USEPA policy and no official endorsement should be inferred.

Permeable Reactive Barriers for Remediation of Acid Mine Drainage

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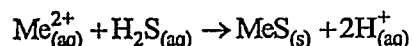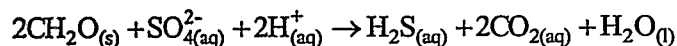519-888-4878
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Permeable reactive barriers are emerging as an alternative to traditional pump and treat systems for groundwater remediation. This technique has progressed rapidly from laboratory bench-scale studies to full-scale implementation over the past decade. Laboratory studies indicate the potential for treatment of a large number of inorganic contaminants, including As, Cd, Cr, Cu, Hg, Fe, Mn, Mo, Ni, Pb, Se, Tc, U, V, NO_3, PO_4, and SO_4. Small-scale field studies have indicated the potential for treatment of Cd, Cr, Cu, Fe, Ni, Pb, NO_3, PO_4, and SO_4. Solid-phase organic carbon in the form of municipal compost has been used to remove dissolved constituents associated with acid-mine drainage, including SO_4, Fe, Ni, Co Cu, Cd and Zn.

Introduction

Over the past decade, permeable reactive barriers have been developed and used to treat groundwater contaminated by inorganic constituents. Permeable reactive barriers are placed in the path of a migrating plume of contaminated groundwater. Reactive materials within the barrier are selected to promote geochemical reactions that result in the destruction or stabilization of the groundwater contaminants. Ideally these materials are sufficiently reactive to treat water for periods of years to decades. Mixtures selected for the attenuation of inorganic species must be designed to maintain their permeability as secondary precipitates accumulate. The barrier design must also ensure that the contaminant will remain immobilized within the aquifer, or can be retrieved with the reactive material following treatment.

Metal Removal by Sulfate Reduction

Biologically mediated reduction of sulfate to sulfide, accompanied with the formation of metal sulfides occurs through the reaction sequence:

$$2CH_2O_{(s)} + SO_{4(aq)}^{2-} + 2H_{(aq)}^+ \rightarrow H_2S_{(aq)} + 2CO_{2(aq)} + H_2O_{(l)}$$

$$Me_{(aq)}^{2+} + H_2S_{(aq)} \rightarrow MeS_{(s)} + 2H_{(aq)}^+$$

where CH_2O represents organic carbon and Me^{2+} represents a divalent metal cation. Biologically mediated sulfate reduction has been used to treat metal cations derived from mining activities in permeable reactive barriers (Blowes et al., 1995, 1998; Waybrant et al., 1995, 1998; Benner et al., 1997, 1999; McGregor et al., 1999). Although these systems are designed to promote the removal of dissolved metals, these barriers also effectively remove sulfate. In laboratory studies, Waybrant et al. (1995) observed sulfate removal at rates of 0.14 to 4.23 mg L^{-1} day^{-1} g^{-1}.

Laboratory studies indicate that many metals, including Ag, Cd, Co, Cu, Fe, Ni, Pb and Zn, are treatable using this approach (Waybrant et al., 1995, 1998). Column experiments, conducted using a range of organic substrates demonstrated the potential to remove a range of dissolved metals at groundwater velocities similar to those observed at sites of groundwater contamination (Waybrant et al., 1995).

In August, 1995, a full-scale continuous reactive barrier was installed in an aquifer downgradient from an inactive mine tailings impoundment at the Nickel Rim mine site, Sudbury, Ontario (Benner et al., 1997). The barrier was installed into a confined bedrock valley by a cut-and-fill technique. The barrier is 15 m long, 4.3 m deep and 3.7 m wide. It is composed of a reactive mixture containing municipal compost, leaf compost, and wood chips to promote bacterial sulfate reduction and metal sulfide precipitation reactions. These organic materials were mixed with pea gravel to attain a permeability greater than that of the aquifer. One meter wide buffer zones containing coarse sand were installed on the up and down gradient sides of the reactive material.

After passing through the permeable barrier, concentrations of SO_4 decrease from 2400 - 3800 mg/L to 110 - 1900 mg/L. The concentrations of Fe decrease from 740 - 1000 mg/L to < 1 - 91 mg/L, and alkalinity values increase from 60 - 220 mg/L (as $CaCO_3$) to 850 - 2700 mg/L (as

CaCO$_3$). A comparison of the equivalents of potential acidity to the equivalents of alkalinity indicate that the water entering the barrier will generate acidity when exposed to atmospheric oxygen. The water leaving the barrier has an excess of alkalinity and will consume acidity when discharged from the aquifer. As a result of the barrier, the plume water will begin to neutralize the pH of the receiving surface-water flow system. Concentrations of dissolved Ni of up to 10 mg/L up gradient of the barrier are decreased to < 0.1 mg/L within and down gradient of the barrier. Enumeration of sulfate-reducing bacteria indicates an abundance of these species within the wall, and elevated numbers in the down gradient aquifer (Benner et al., 1997).

In March 1997, a pilot-scale, compost-based reactive barrier was installed at an industrial site in Vancouver, Canada (McGregor et al., 1999). The barrier was installed in the path of a plume of groundwater containing Cd, Cu, Ni, Pb and Zn. The barrier was installed by trenching using biodegradable slurry. Dissolved Cu concentrations were observed to decrease from 300 mg/L to <5 mg/L within the barrier. The concentrations of Cd, Ni, Pb and Zn showed similar decreases, with effluent concentrations generally below instrument detection limits.

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Long-Term Performance Monitoring of a PRB for Remediation of Chlorinated Solvents and Chromium

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Permeable reactive barriers (PRBs) are an emerging, alternative *in situ* approach for remediating contaminated groundwater that combine subsurface fluid flow management with a passive chemical treatment zone. In the last few years, there has been extensive research conducted to improve our understanding of the mechanisms and kinetics of the transformation reactions responsible for the removal of contaminants from the aqueous phase in such *in situ* treatment systems. The few pilot and commercial installations which have been implemented have proven that passive permeable reactive barriers can be a cost-effective and efficient approach to remediate a variety of different compounds. However, in all of the pilot and commercial installations to date there has been very little data collected or research focused on the long-term performance of these *in situ* systems, particularly with respect to the build-up of surface precipitates or bio-fouling.

A detailed analysis of the rate of surface precipitate buildup in these types of passive *in situ* systems is critical to understanding how long these systems will remain effective. Different types of minerals and surface coatings have been observed to form under different geochemical conditions which are dictated by the composition of the permeable reaction zone and aquifer chemistry. Microbiological activity impacts are also important to understand and better predict how long these systems will remain effective in the subsurface.

Continuous Wall Emplacement

A permeable *in situ* subsurface reactive barrier composed of 100% granular zero-valent iron (ZVI) was installed in June, 1996, at the U.S. Coast Guard Support center near Elizabeth City, North Carolina to treat overlapping plumes of chromate (Cr(VI)) and chlorinated solvent compounds (trichloroethylene (TCE), cis-ichloroethylene (c-DCE), and vinyl chloride (VC)). Concentrations in excess of 10 mg/L Cr and 19 mg/L TCE had been detected in the groundwater at the site since 1991. The wall was emplaced using a continuous trenching machine. The continuous trencher excavates native soil and allows the iron to be emplaced in one continuous operation. Excavated aquifer materials were brought to the surface by an excavating belt, and then conveyed to the side of the machine. An estimated 3.2 m^3 of iron-filings were emplaced per linear meter and about 280 tons of iron was installed. The installation was completed during a 6 hour period on June 22, 1996. The PRB is 46 m long, 7.3 m deep and 0.6 m wide and oriented perpendicular to groundwater flow.

Wall Emplacement Verification

Wall emplacement was verified using a conductivity probe manufactured by Kejr Engineering, Inc that was advanced through the soil/iron interface using a Geoprobe™ . The tool provides real-time, specific conductance data versus depth on a portable computer. The radius of influence of the probe is 2-3 cm. The data was used to identify the location of the plume, the outlines of where the iron was emplaced, and the density of packing of the iron filings within the aquifer. Conductivity values greater than 100 mS/m indicate the presence of the granular iron. Differences in conductivity between the aquifer sediments and the iron filings were as much as 2 orders of magnitude, making this a very useful tool in locating the relatively thin wall (0.6 m). Data collected thus far indicates a wall thickness of 45 cm, or 15 cm less than the designed thickness of 60 cm. Other measurements have ranged from 48 to 55 cm.

Monitoring Network

Performance monitoring entails the following: sampling of 10-5 cm dia PVC compliance wells and 15 multi-level samplers (7 to 11 sampling points per sampler) arranged in three transects perpendicular to the wall for the following constituents: TCE, cis-DCE, vinyl chloride, ethane, ethene, acetylene, methane, major anions, metals, Cr(VI), Fe(II), total sulfides, dissolved H_2 , Eh, pH, dissolved oxygen (DO), specific conductance, alkalinity, and turbidity.

Geochemical Indicator Parameters

Ferrous iron concentrations within the wall increase from background levels within the aquifer of less than 0.5 mg/L to as much as 14.8 mg/L but are variable with depth, location and time. Total iron concentrations are similar to ferrous iron values indicating most of the soluble iron is in the ferrous form. Within 1.5 m downgradient, ferrous iron concentrations persist as high as 2.2 mg/L. Eh values within the wall are as low as -600 mv but generally range from -250 to -550 mv, whereas upgradient Eh ranges from 250 to 450 mv. Upgradient pH ranges from 5.7 to 6.5, whereas within the wall the pH is generally between 9 and 10.7. DO values within the aquifer range from 0.2 to 2.0, whereas within the wall DO is generally less than 0.2. Dissolved hydrogen increases from background concentrations of less than 10 nMol to greater than 1000 nMol. These data are consistent with the effects of the iron corrosion reaction. The following equation shows that the oxidation of the iron filings would be expected to generate ferrous iron and dissolved hydrogen, decrease Eh and increase pH:

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$$
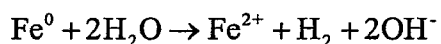
Geochemical conditions within 1.5 m downgradient of the wall show increasing reducing conditions over time, indicating that a "redox front" may be moving downgradient from the wall and the area affected by reducing conditions may increase over time.

Wall Performance: Contaminant Removal

The center of the Cr(VI) plume resides between 4.5 and 5.5 m below ground surface while the extent of the plume ranges from 4 to 7 m below ground surface. Cr(VI) concentrations decline from upgradient values as high as 5.1 mg/L to less than detection limits (<0.01 mg/L) within the first few centimeters of the wall. No chromate is detected downgradient of the wall.

Under the highly reducing conditions which prevail within the wall, the reduction of Cr(VI) to Cr(III) is predicted and the subsequent formation of an insoluble precipitate is formed as shown below:

$$Fe^0 + CrO_4^- + 4H_2O \rightarrow (Fe_x Cr_{1-x})(OH)_3 + 5OH^-$$
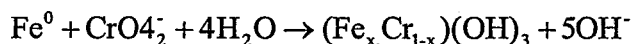
Geochemical modeling calculations indicate that this precipitate should form and support Cr(III) aqueous concentrations less than 0.01 mg/L. Cr (III) has been detected on the surface of the iron in a few cores using x-ray photoelectron spectroscopy (XPS) analysis. Cr has also been detected in these same samples using scanning electron microscopy with energy dispersive x-ray analysis (SEM-EDS) and appears in association with iron as surface coatings on the iron filings.

The vast majority of the multi-layer sampling ports show reduction of the chlorinated volatile organic compound (CVOC) concentrations to less than North Carolina (Department Environmental Quality) regulatory target levels (5 mg/L, TCE; 70 mg/L, c-DCE; 2 mg/L VC). With the disappearance of the TCE, c-DCE and VC, there has been a steady increase in detectable ethane, ethene, and acetylene. These data indicate that the organic compounds are degrading via both reductive dechlorination and beta elimination pathways.

Analysis of Emplaced Iron

Limited mineralogic analyses of cores have been completed. Due to increased pH within the wall, there is a shift in equilibrium form a bicarbonate to a carbonate dominated system. Analysis of total inorganic carbon to evaluate precipitation of likely carbonate phases (e.g. siderite [FeCO_3], calcite [CaCO_3]), shows increases in inorganic carbon within the iron compared to the upgradient aquifer sediments. This is true for both the upgradient and downgradient interfaces, but differences are greater for the upgradient cores.

The presence of a large reservoir of iron and favorable pH and substrate availability conditions may favor the activity of iron and sulfate reducing bacteria and methanogens. This enhanced activity may favorably influence zero-valent iron reductive dehalogenation reactions through favorable impacts to the iron surface or through direct microbial transformations of the target compounds. However, this enhancement may come at the expense of faster corrosion leading to faster precipitate buildup and potential biofouling of the permeable treatment zone. Increases in microbial biomass have been detected at the upgradient and downgradient wall interfaces.

The most ubiquitous mineral phases observed thus far are amorphous iron (oxy)hydroxides, calcite, siderite, and possibly green rust (general stoichiometry of $[Fe^{2+}_4 Fe^{3+}_2 (OH^-)_{12}]^{2+} \cdot [SO_4^{2-} \cdot H_2O]^{2-}$). The corrosion layer is greatest (20-25 um) within the first 5 cm and decreases significantly (<5 um) within 20 cm of the upgradient interface. These observations have been made with cross-sectional SEM-EDS and additional studies are underway.

Summary

Chromium is removed from the groundwater to less than detection limits (<0.01 mg/L) and considerably less than regulatory target levels (0.1 mg/L). This is accomplished via redox reactions accompanied by precipitation processes due to the corrosion of the iron. Likewise there is reduction in CVOC concentrations to less than regulatory limits where these compounds are entering and being treated by the iron wall.

Acknowledgments

Long-Term Performance Monitoring of Permeable Reactive Barriers at DOE Sites

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A permeable reactive barrier was installed to destroy chlorinated hydrocarbons at the Department of Energy's (DOE) Kansas City Plant. In the Feasibility Study, it was predicted that mineral precipitation would not be a problem for a minimum of five years. It is hoped, of course, that the barrier will last much longer. Nevertheless, most scientists believe that barriers will eventually require regeneration or retrieval. Indeed, where removal of uranium with Fe^0 is concerned, as at deployments on the Oak Ridge reservation, some believe that barriers will have to be removed or re-oxidation and remobilization will occur. When Fe^0 is used in an *in situ* barrier, corrosion and mineral precipitation alter the surface composition. Pilot studies have shown that compositional changes decrease the reactivity of the iron and mineral precipitation decreases flow through the barrier [McKenzie et al 1997].

One field test exhibited significant clogging within 6 months of operation [Korte et al. 1997]. The influent side of the media was solidly cemented and sampling of the media revealed the presence of a diverse microbial population. Clearly, cost-effective monitoring in conjunction with predictive capability to determine when barrier failure is imminent are needed. For these reasons, the DOE, the Department of Defense (DOD), and the EPA (EPA) have embarked on a joint project to determine cost-effective long-term monitoring strategies. In this presentation, observations from field installations are summarized, and a biogeochemical conceptual model, to be used as a basis for developing long-term monitoring strategies, is proposed. A brief discussion of hydraulic monitoring concepts is also included.

Water Quality

Water quality data from Fe^0 barriers is not always consistent with respect to pH, dissolved oxygen (DO), alkalinity, and concentrations of cations and anions. At Hill Air Force Base (AFB), the pH increased from 7.5 to >9. Similarly, pH was significantly higher within the Fe^0 than in the influent in installations at Sunnyvale, CA; Lowry AFB, CO; and Elizabeth City, NC. In contrast, the pH remained near neutral (from ~ 6 to ~7) at the Portsmouth Gaseous Diffusion Plant (PORTS) in Ohio [Liang et al. 1997].

At Ports, significant clogging occurred within the Fe^0-medium, forcing the system to cease operation after 6 months. A significant decrease in SO_4^{2-} concentration was also observed with the effluent SO_4^{2-} between 125 to 175 mg/L versus an influent concentration of 400 mg/L. The groundwater at Ports contained iron oxidizers, sulfate reducers, anaerobic heterotrophs, and iron reducers at levels of 1 to 100/mL. In contrast, after 1 year of operation of the Fe^0 barrier at the Borden site, samples did not show biological growth, mineral precipitation, or alteration of the iron [Matheson 1994, O'Hannesin and Gillham 1998]. At most field sites, however, precipitates are detected. Precipitate formation was observed at the top of the reactors at the SGL Printed Circuits site in New Jersey, at the Lowry AFB site in Colorado, and at the Y-12 site in Tennessee. At the Lowry site, total alkalinity, Ca^{2+} and SO_4^{2-} concentrations rapidly decreased along the reactor flow path [Edwards et al. 1996]. At Hill AFB, precipitates of iron and calcium carbonate accounted for a 14% reduction in porosity within a few months. A lower annual porosity reduction (0.5% porosity loss) was estimated after 10 months of operation at the Denver Federal Center site [McMahon 1997].

A Conceptual Model

The variable results from the field indicate that an increased understanding of both chemical and microbial reactions should permit more accurate predictions regarding clogging and biogeochemical impacts on Fe^0 barrier performance. In considering a conceptual model, it is assumed, as a first approximation, that all reactions reach a pseudo-equilibrium.

The chemical aspects of a conceptual model can be bounded by the following hypotheses:

- An elevated DO in groundwater will be a major factor contributing to the corrosion and plugging of a reactive barrier due to the precipitation of ferric oxide/hydroxide at the up-gradient interface.

- Groundwater with limited buffering capacity will exhibit a high pH in the Fe^0 barrier, thus suppressing microbial activity, which, in turn, will result in little risk of biofouling.

- Groundwater with a high bicarbonate buffering capacity will result in near-neutral pH in the Fe^0 and greater risk of fouling/clogging from precipitation of metal sulfides and carbonates.

- Natural organic matter will compete for iron and oxide/ hydroxide surfaces; thus inhibiting reductive surface reactions with contaminants.

- When Fe^0 contacts groundwater, oxidation-reduction, mineral precipitation, and associated equilibrium reactions occur. Mixed oxides (e.g., green rusts) that incorporate different types and amounts of anions (Cl^-, SO_4^{2-} or CO_3^{2-} etc.) may form. Transformation of one mineral to another, such as green rust to ferric oxyhydroxide or to iron sulfides, also will occur.

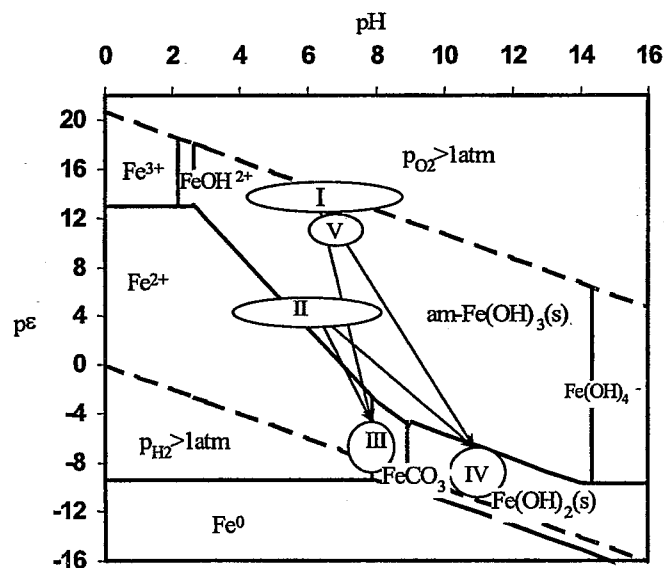Using pH and pe, Fig. 1 demonstrates that different iron minerals are observed depending on the nature of the influent groundwater and the corresponding effluent from the Fe^0 barrier. Thus, the amount of precipitation produced depends on the characteristics of the influent groundwater (shown in regions I and II in Fig. 1) as well as the resulting effluents (as region III and IV).

Typical groundwater pH ranges from ~5 to ~8. High DO groundwater is illustrated in region I in Fig. 1 and low DO in region II. As groundwater passes through the Fe^0, DO will be consumed rapidly, decreasing the redox potential to about –400 to –600 mv as illustrated in regions III and IV.

Precipitation as Influenced by Dissolved Oxygen

Region V in Fig. 1 typifies the condition under which oxidative precipitation of ferric oxides may cause clogging at the upgradient interface. The aerobic oxidation of Fe^0 results in the precipitation of amorphous iron oxide:

$$Fe^0(s) + 1\frac{1}{2}H_2O + \frac{3}{4}O_2 \rightarrow Fe(OH)_3(s)$$
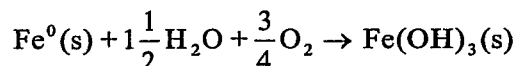
When treating water with a high DO and a neutral pH, orange precipitates typical of oxidized iron have been observed in the Fe^0-medium in bench and pilot-scale studies [Liang et al. 1997, McKenzie et al. 1997, Shoemaker et al. 1995]. Under neutral pH conditions, the solubility of ferric hydroxide is low and its precipitation is expected.

Thus, the influent DO determines the amount of ferric oxide produced at the interface to the Fe^0-barrier. For every ¾ mole of oxygen consumed, 1 mole of iron oxide is produced (Eq. 1). Thus, if a groundwater contains 4 mg/L (0.125 m$\underline{M}$) DO, the molar concentration of ferric hydroxide generated could be 0.17 m$\underline{M}$ (18 mg/L). Assuming that water enters the Fe^0 media through a cross-sectional area of 1 ft² (0.09 m²) at a flow rate of 0.1 gal/min (0.39 L/min), within 6 months the amount of ferric hydroxide generated could approach 2 kg and form a 1.3-cm-thick plug (assuming a porosity of 0.5 and a density of 3 g/cm³).

System pH and Alkalinity

A poorly buffered groundwater will show a large pH increase, characterized by region IV in Fig. 1. Most laboratory tests have been conducted in weakly buffered solutions, and the pH observed is typically >9 [Gillham and O'Hannesin 1994]. Examples from the field include Hill AFB and a site in Sunnyvale, California, where a high pH typical of low alkalinity groundwater was observed [Shoemaker et al. 1995].

As noted previously, alkalinity will largely determine the pH of the barrier effluent. Groundwater with a limited buffering capacity will show an increase, and groundwater containing high alkalinity and/or high SO_4^{2-} will have a near-neutral pH as in region III, Fig. 1. Although carbonate species are the major contributors to groundwater alkalinity, redox and microbial reactions could produce species that

Figure 1. pH-pe diagram for the system $Fe-CO_2-H_2O$, illustrating estimated pH, pe, and the iron mineral precipitates that correspond to the type of influent and effluent groundwater chemistry for an Fe^0 reactive barrier. The solid phases are am-$Fe(OH)_3$ (amorphous ferrous hydroxide), and $FeCO_3$ (siderite), $Fe(OH)_2$ (ferrous hydroxide), and Fe^0. Lines are calculated based on total carbonate species at 10^{-3}M, ferrous and ferric iron at 10^{-5}M. (Adapted from Strumm and Morgan 1996).

neutralize H^+. For example, ferric oxide species formed from Fe^0 oxidation and sulfide species from SO_4^{2-} reduction can increase alkalinity. Microbial SO_4^{2-}-reduction can cause fouling and clogging from mineral precipitation as well as from the growth of the bacteria.

Water quality changes at the PORTS site provided direct evidence of sulfate-mediated biogeochemical reactions. The influent SO_4^{2-} concentration decreased across the Fe^0 medium, while pH remained near neutral. The change in Fe(II) concentration with time coincided with that of alkalinity. The cause of the alkalinity increase has been attributed to the presence of dissolved ferric and ferrous hydroxide species, sulfides, and titratable organic compounds produced by SO_4^{2-}-reducing bacteria. The simultaneous decrease of Fe(II) and alkalinity indicated the precipitation of siderite within the medium.

Hydraulic Monitoring

Hydraulic monitoring is as important as geochemical monitoring when evaluating barrier performance. Thus, this project has also focused on determining the type of hydraulic testing that should be performed. Various types of flow meters have been used in and around barriers. The colloidal borescope, which uses natural colloid flow within the barrier as a means of measuring groundwater flow rate and direction, has been used at several DOE sites. Directional data with a heat-pulse flow meter at the Kansas City Plant, however, showed little correlation with data from the colloidal borescope or with the potentiometric surface. The borescope, while it provides consistent data, can be difficult to use within a barrier because there are so many finely divided iron particles floating within the well bore. Continuous water-level measurements, therefore, appear to be the most useful hydraulic monitoring method. Additional testing at a variety of sites should yield specific recommendations regarding which procedures are appropriate.

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Demonstration of Permeable Reactive Barriers for Groundwater Remediation: Status and Preliminary Results of the Fry Canyon Project

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An abandoned uranium (U) ore upgrading facility in southeastern Utah, known as the Fry Canyon site, was selected as a long-term demonstration site to assess the performance of selected permeable reactive barriers (PRBs) for the removal of U and other trace elements from groundwater. PRBs consist of reactive material placed in an aquifer for the purpose of immobilizing, destroying, or rendering a contaminant less toxic or mobile. Previous PRB installations targeted primarily organic contaminants.

Project partners include the USEPA (USEPA), Utah Department of Environmental Quality, and U.S. Geological Survey. Project funding was provided by the USEPA. Objectives of the project were: (1) hydrologic and geochemical site characterization prior to barrier emplacement; (2) design, installation, and operation of selected materials;

and (3) evaluation of barrier(s) performance for site remediation and economic viability.

Three PRBs were installed in 1997 using funnel and gate construction techniques. Reactive materials demonstrated are zero valent iron (ZVI), amorphous ferric oxyhydroxide (AFO), and phosphate (PO_4). Uranium concentration in the aquifer ranged from 60 micrograms per liter (mg/L) in water from a background well to 20,700 mg/L in water beneath the tailings. Uranium reduction ratios (input U concentration/PRB U concentration) were calculated for all water samples collected from each PRB. Initial results indicate that the ZVI PRB is most efficient in removing U from groundwater (>99% removal rate); however, U removal efficiencies in the PO4 and AFO PRBs also are high (>90% removal rate).

An Overview of Installation Methods for Permeable Reactive Barriers

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In situ permeable reactive barriers (PRBs) for groundwater remediation have been proven to be a cost effective alternative to conventional groundwater treatment. Various configurations and installation methods have been implemented to install PRBs into the subsurface at various depths. Innovative configurations have evolved to reflect site specific parameters such as site geology, hydrogeology and contaminants distribution. Various conventional geotechnical construction methods have been adapted to accommodate installations involving reactive materials.

Configurations

Various PRB configurations have been implemented to ensure complete plume capture and remediation. A continuous permeable wall configuration distributes the reactive material across the entire path of the contaminated groundwater. This configuration is least sensitive to complexities in the flow field and does not significantly alter the natural groundwater flow path.

In a funnel and gate configuration, the contaminated groundwater is directed by low permeability funnels towards a permeable treatment zone or gate. The funnel sections could consist of sheet piling (which eliminates the removal of soil and reduces the soil disposal cost), or slurry cutoff walls. Depending on the type of slurry wall, some portion of the excavate soil may be incorporated into the wall, however, soil disposal costs must be taken into account for these types of funnels. The funnel and gate system must be keyed into a lower hydraulic conductivity layer. Taking take into consideration aquifer heterogeneity and to minimize groundwater mounding, a low funnel to gate ratio is preferred. In order to assure complete capture of the plume, the length of a funnel and gate system is typically 1.2 to 2.5 times the plume width depending on the funnel to gate ratio and the number of gates. This system has a larger water flux per unit of reactive material area. The funnel and gate configuration allows for reactive material to be more easily replaced, however, field experience indicates funnel and gates are more susceptible to hydraulic uncertainties which cause by pass of flow around the system.

A slight adaptation of the typical funnel and gate is the *in situ* reactive vessel, where the funnels or collection trench collect the water and as a result of hydraulic head build up on the upgradient side, causes the groundwater to flow through the buried vessel. A GeoSiphon™ is a innovative configuration developed by the Westinghouse Savannah River Company which is designed to passively induce contaminated groundwater flow through a permeable treatment system at an accelerated rate via a siphon, taking advantage of the natural hydraulic head difference between two points. Once the siphon is established the passively induced flow draws the contaminated groundwater towards and through the treatment cell, treats the groundwater and is subsequently discharged to a lower hydraulic head at ground surface or surface water.

The theoretical amount of reactive material needed in a PRB is independent of treatment system configuration, since any configuration will have to treat the same mass flux. An exception may be when a minimum amount of reactive material is required due to construction limitations.

Construction Methods

The choice of construction method will depend on the depth of installation, site geology and amount of reactive material requiring placement. Recent papers discussing various construction methods are given in Gavaskar, et al. (1998), Day et al. (1999), MSE (1996) and Rummer and Ryan (1995). Conventional excavation and replacement methods are typically utilized at shallow depths (less than 35 ft) and are typically less expensive than those implemented deeper into the subsurface.

Shallow Methods

Several construction methods are available to accommodate these various configurations at shallow depths. At depths typically less than 35 ft, methods generally involve

excavation and replacement procedures. The least expensive trenching method would be backhoe trenching which could be implemented if the formation soil does not cave in. However, the limitation would be the excavation width. A continuous trenching machine, which is currently limited to depths of less than 30 ft, allows for simultaneous excavation and backfilling without an open trench. It allows for very rapid installation, however, it has considerably large equipment and slightly higher mobilization costs. Several trenching contractors have installed these systems, with costs ranging from $200 to $400 per linear foot. Another common installation method is cofferdam or sheet pile excavation boxes which are formed and braced using interlocking sheet piling. The sheet piling maintains the dimensions of the treatment zone during excavation and backfilling. After backfilling is complete, the sheet piling is removed and the groundwater is allowed to flow through the treatment zone. Cost for this installation average about $80 ft². Trench boxes, like sheet piling are used to maintain trench integrity during excavation and backfilling operations and range about $10 to $20 per ft². Auger holes have also been utilized to install treatment zones. Rotating a continuous flight of hollow stem augers into the required depth, the reactive material can be placed through the auger stem as the augers are removed. These treatment zones can be created by overlapping holes or in well arrays where two or more rows are required.

Deep Methods

For deep installations typically greater than 35 ft, excavation and replacement can be costly. Costs are often influenced by the need to excavate to considerable depths through uncontaminated soil before reaching the plume.

Caisson installation involves driving a large circular steel caisson into the ground and augering our the native material. The caisson is then backfilled with a reactive material and removed. Overlapping or tangential caisson emplaced treatment zones can be used to create a larger permeable treatment zone. However, the overlapping caissons causes wastage of iron ranging from 10% to as high as 30%. Caisson implementation averages about $200 per vertical foot.

A mandrel or H-beam is a hollow steel beam with a disposable shoe at the leading edge which is driven into the ground to create a thin continuous treatment zone. Once the mandrel reaches the maximum depth of the treatment zone the reactive material is placed inside the mandrel and the disposable shoe is removed. This process is then repeated creating a continuous zone of reactive material. In previous applications, parallel treatment zones were created to provide sufficient reactive material and to reduce the risk that the contaminants would not come in contact with the reactive material. This installation method ranges from $10 to $20 per ft².

Another installation method that has been proposed at several sites, but has not been used to date, is ground freezing which has been implemented in the construction industry for many years. This involves the use of refrigeration to convert in situ pore water into ice. The ice acts as a bonding agent which fuses together particles of soil to increase the strength of the mass and make it impervious. Excavation can be performed safely inside the barrier of water-tight frozen earth with conventional excavation equipment.

Deep Construction Methods Employing Biodegradable Slurry

Other deep installation methods require that the reactive materials be carried in a biodegradable slurry (bioslurry), usually guar. These methods have been employed in the construction industry for years, and are currently being modified to implement PRBs along with various reactive materials deep into the subsurface. As part of pre-construction activities, tests to determine that the site water chemistry is compatible with the reactive material and bioslurry mixture and to assure that the bioslurry breakdowns over a suitable time period at groundwater temperatures should be undertaken. Additional testing should also be undertaken to determine the effectiveness of the reactive material once it has been in contact with the bioslurry.

A bioslurry trench installation is similar to constructing a conventional impermeable slurry wall. As the trench is excavated, bioslurry provides stability to the trench walls, and the reactive material is placed via a tremmie tube into the trench. There should be minimal contact between the reactive material and bioslurry. The method of circulation of the breaker/enzyme plays a critical role in assuring complete breakdown of the bioslurry. Costs for implementing this installation method range from $15 to $25 per ft².

Vibrated beam technology has been used for years to install thin impermeable slurry walls and recently has been adapted to inject reactive material and bioslurry. The large I-beam is driven into the subsurface and as the beam is vibrated out, a reactive material and bioslurry is pumped into the formation filling the void created by the beam. This process is then repeated and several lines in parallel could provide the required amount of reactive material. This technique could cost on the order of $10 per ft².

Deep soil mixing has been suggested where the reactive material is mixed with biodegradable slurry and pumped to the mixing augers while they are being advanced slowly through the soil. Over time the bioslurry breakdowns allowing the groundwater to flow through the reactive material and aquifer mixture or treatment zone. High costs are associated with mobilization and demobilization for deep soil mixing. Costs typical range from $75 to $120 per cubic yard.

Two other deep installation methods that have been successfully demonstrated in the field are jetting and vertical hydrofracturing. Jetting uses high pressure to inject fine

grained reactive material into the natural aquifer formation. The jetting tool is advanced into the formation to the desired depth, then the reactive material and bioslurry is injected through the nozzles as the tool is withdrawn. Either columnar zones or diaphragm walls can be created. Jetting may cost on the order $75 per vertical foot for columnar walls. Vertical hydrofracturing uses a specialized tool to orient a vertical fracture and initiate the fracture process. The tool is placed to the desired depth through a borehole and the interval for fracturing isolated by packers. The reactive material and bioslurry in then pumped under low pressures into the formation to form a thin vertical plume along the line of the induced vertical fracture.

Construction Uncertainties

Many unforeseen conditions have been encountered during PRB construction. These issues can pertain to unexpected "complexities" in geological formation or complications with the construction technique itself. These unanticipated issues have included:

- compaction or densification of the aquifer material during the vibration of equipment such as caisson or sheet pile;

- compaction effects on the aquifer soils when using mandrel, I-beam, jetting and vertical hydrofracturing;

- flowing sands with continuous trenching requiring additional passes of the trencher;

- slurry wall flows into the excavated void created for the reactive material;

- smearing of clay and sand zones during gate construction, resulting in inadequate flow through the treatment zone;

- slow breakdown of bioslurry used in jetting, deep soil mixing, vertical hydrofacturing and bioslurry trench;

- sufficient flushing of the bioslurry to prevent high biological activity zone downgradient;

- insufficient reactive material injection during jetting.

These problems are addressed during PRB construction, on a site specific basis, but have added time and costs to system installation. However, these "lessons learned" have helped improve the cost effectiveness of subsequent PRB installations, making the technology an even more attractive remedial alternative.

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Mechanisms in *In Situ* Thermal Remediation

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Many of the physical properties of organic contaminants, as well as the properties of porous media, limit the recovery of contaminants through techniques such as pump and treat or soil vapor extraction. Remediation techniques that rely on the addition of chemicals suffer from the lack of the ability to mix the chemicals with the contaminants in the subsurface, and from limitations on recovering the chemicals. The physical properties of fluids and their interactions with soil will control their movement in the subsurface, as well as their recovery. All of these properties are temperature-dependent. In addition, various types of liquid and vapor movement can be created in porous media due to temperature gradients.

Understanding these temperature effects and their relative magnitudes is important in understanding how *in situ* thermal remediation processes can be used to enhance the recovery of organic contaminants. For volatile organic compounds, which includes fuels such as gasoline and diesel and chlorinated solvents, the main mechanism for enhanced recovery is the increased vapor pressure with temperature which allows these compounds to be recovered in the vapor phase. Enhanced solubility and de-creased adsorption at higher temperatures will also contribute to the recovery of these chemicals.

The recovery of semivolatile and (essentially) nonvolatile oils can be enhanced at higher temperatures through viscosity reduction, increased relative permeability, and decreased capillary forces. These changes in physical properties allow oils to be displaced in the liquid phase when there saturation is greater than residual saturation, and also tend to decrease the amount of residual saturation. Field experience demonstrates that even semivolatile organic compounds can be distilled at significant rates when high temperatures and low vapor phase pressures conditions are created in the subsurface.

Ongoing research shows that naturally existing soil microbes can survive temperatures of 100°C, and potentially can degrade the small amount of contaminants that remain after a thermal remediation. Also thermophysical reactions have been found to partially or fully oxidize some organic contaminants. These biological and thermophysical process can make contaminants easier to recover, or destroy them *in situ,* and contribute to the cost effectiveness of thermal remediation processes.

Remediation of Soils and Groundwater Using Steam Enhanced Extraction

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Soil and groundwater contamination by non-aqueous phase chemicals is a problem of international importance. The concern over these chemicals is due, in part, to their potential to contaminate groundwater for centuries to come. Decades of work in the area of *in situ* remediation has resulted in few successes. But *in situ* thermal techniques have been gaining popularity, both in the U. S. A. and internationally, due to their robustness. Part of the success of such techniques is from the fact that once the soil-water-NAPL system is heated to the boiling point of water, equilibrium thermodynamics requires complete NAPL vaporization. Thus, if coupled with active soil vapor extraction, the removal rate of the liquid chemical is determined by the relatively fast heat transfer rate, not the slower mass transfer rate. In addition, concentrations of chemicals that tend to partition into the vapor phase can be easily decreased to drinking water standards through depressurization, electrical heating or radio frequency heating if the soils are at the water boiling point.

These mechanisms, plus enhanced NAPL mobility with increasing temperature, can be easily be exploited by steam enhanced extraction (SEE). In SEE, steam is injected into the subsurface to heat the target zone of contamination to the boiling point of water while actively pumping water, NAPL and vapors from other wells. This is continued until the zone is sufficiently heated. Thereafter, the steam injection pressure and extraction well vacuum are varied to induce pressure changes in the heated zone. During periods of decreasing pressure (depressurization), the temperature decreases to maintain thermodynamic equilibrium between the steam and the water in the soil, giving up energy to drive the vaporization of interstitial water. This *in situ* boiling occurs in a manner relatively independent of the permeability thus allowing convective fluxes from lower permeability regions. Thus, mass transfer limitations are relaxed and recovery rates are increased. After the pressures in the soil have reached nearly steady values, the pressures are increased to recharge the soil with energy through the condensation of steam. This pressure cycling continues until the recovery rates and extracted fluid concentrations decrease to low values.

Two field examples of this process are briefly discussed. The first is the Gas Pad at Lawrence Livermore National Laboratory. The subsurface geology was of alluvial origin, with layers of high permeability interspersed with clays and clayey silts. The horizontal correlation of the high permeability layers was moderate except for a thick gravel layer found below the water table from about 35 m (140 ft.) to 42 m (150 ft.). This gravel layer was found in each well surveyed. The gasoline was detected as a second phase in an area about 50 m (150 ft.) in radius. The vertical distribution ranged from 17 m (50 ft) to about 45 m (137 ft.), with significant spreading due to major groundwater elevation fluctuations. Indeed, separate phase gasoline was found in the deep water-bearing zone nearly 8 m below the water table. This situation rendered others technologies such as ambient temperature vacuum extraction to be impracticable, and groundwater extraction to be time-prohibitive. There were two major flow zones at this site: the deep gravel layer and an upper unsaturated zone consisting of intermingled sands, silts, clays and gravels. A contaminated clay layer of variable thickness separated the two permeable zones.

Six injection wells were placed around the perimeter of the area contaminated by separate phase gasoline; three recovery wells were installed near the center of the plume. The injection wells were constructed to allow separate steam injection into the upper and/or lower permeable regions. The recovery wells were completed over the entire height of the contaminated zone. To monitor the subsurface temperatures, 11 temperature observation wells were placed throughout the site.

The above ground equipment included a boiler fired by natural gas, a flat-plate condenser cooled by water recirculated though a cooling tower, cooling heat-exchanger for the liquids pumped from the subsurface, separation tanks, water treatment facilities, and air treatment. Automotive internal combustion engines were used to oxidize the recovered hydrocarbons in the air exiting the condenser and to serve the purpose of the vacuum pump.

During the two months preceding steam injection, 3-phase electrical heating was conducted during off-hours. A total of 202 Mw-hrs of electrical energy was dissipated in predominantly clay-rich zones.

During the first 37 days of operation, steam was injected first into the lower gravel layer below the water table for two weeks. The total electrical energy input was surpassed with steam after the first three days of injection. Steam broke through at the recovery wells after about 10 days of injection. The steam was injected on a variable schedule thereafter into the upper zone and/or lower zone to target lower temperature regions. At the end of 37 days, operations ceased for 75 days. Steam injection resumed for a second pass after 9 days of groundwater extraction and vacuum pumping. The steam injection schedule was periodic with periods of steam pressurization and de-pressurization. Steam was injected a total of 21 days during this 46 days of gas and groundwater extraction.

The recovery rates observed during the second pass were highest before steam injection began as the extraction system recovered high-concentration gases evolved during 45 days of down-time conductive heating. Thereafter, periodic peaks in the recovery rates were observed corresponding to times when steam injection ceased and depressurization began. The 2nd pass was terminated due to permitting restrictions on the boiler while recovery rates remained high and may have continued with additional cycles of steam injection. During the next 80 days, soil samples were collected, the steam boiler was taken from the site, and additional electrical heating wells were installed. The treatment system was shut down during this period.

The soil concentrations found after the second pass showed that, in general, gasoline was effectively removed from the hot steam-bearing zones and concentrations were significantly reduced in the low permeability zone separating the upper and lower permeable units. An estimate of 2840 liters (750 gallons) of gasoline remained in the soil after the end of the second pass based on the soil concentrations after the second pass.

The recovery rates during the final phase were significant at the beginning of pumping, but the rates fell with time, with magnitudes much less than those observed during the second pass. Some improvement in the recovery rates were achieved by converting upper zone injection wells into vapor recovery well. However, little could be done to increase recovery rates during the final few days of operation - including electrical heating. Regardless, an additional 3800 liters (1000 gallons) of gasoline were recovered in this final phase before the recovery rates dropped to small values.

Subsequent gas and water sampling is showing decreasing concentrations of gasoline components with time without additional pumping, implying that there is no separate phase gasoline remaining at this site. Ethybenzene, toluene, and xylene concentrations in the water have dropped to below regulation limits. Benzene concentrations continue to decrease. Hydrocarbon-degrading biological activity was found in the zones subjected to steam temperatures, indicating that the application of steam did not leave the site sterile. The culture make-up however, has been dramatically altered. No further treatment at that site was required.

The second demonstration of interest is Site 5 at Alameda Point (formerly Naval Air Station Alameda) in California. This site is the location of an underground waste solvent tank that has leaked a mixture of solvents into fill soils only 3 m. (10 feet) below the ground surface. This site presented special challenges for SEE due to the shallow depth and complex NAPL chemistry.

The aboveground equipment included a boiler fired by propane, an air-cooled condenser, a cooling tower providing the cooling for the liquids pumped from the subsurface, separation tanks, and carbon for water treatment and air treatment. Sealed ring vacuum pump placed downstream of the air-cooled condenser provided up to 20 inches of Hg vacuum at the well.

Six injection wells were placed around the perimeter of the area contaminated by nonaqueous phase solvents; one recovery well was installed near the center of the plume. The injection wells were constructed to allow separate steam injection into the upper vadose zone and/or lower saturated regions. The recovery well was completed over the entire height of the contaminated zone. Two hundred and seventeen theromocouples were placed throughout the site to monitor subsurface temperature distributions.

Steam was injected for 70 days during this demonstration. After temperatures began to increase near the extraction well, separate phase solvents began to flow from the subsurface. After a period of about 15 days of separate phase solvent pumping, the separate phase flow stopped and recovery was dominated by vaporization. After 18 more days of steady flow, vaporization rates dropped to low values and cyclic steam injection began. Recovery rates increased again to high values during the first cycle, then decreased sequentially with each additional cycle. Nearly 2000 liters (528 gallons) of NAPL were collected in drums and sent out for disposal during the demonstration. The TCE was removed primarily in the vapor phase (~200 kg), with significant mass also measured in the extracted water (22 kg) and NAPL (18 kg).

Near the end of the demonstration, TCE and other solvents concentrations in the extracted water decreased to background values. Salt concentrations and oxygen 18 isotopic values in the extracted water also indicated that the water came from outside of the demonstration area. Since the goal of this demonstration was source removal to support natural attenuation as the final remedy, the demonstration was considered to be highly successful.

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These projects and others currently underway have shown the effectiveness of SEE to remove NAPLs from soils and their soluble fractions from groundwater. The scientific basis of the process is quite well-defined and the *in situ* application is surprisingly robust. The keys to successful implementation were found to be appropriate monitoring to control the locations and rates of steam injection, and planning for the various phases of recovery including start-up, high NAPL rates, high vaporization rates and cyclic operation. This planning includes modeling to ensure proper sizing of all treatment equipment, design for flexibility of operation, and measurement locations to provide confidence in monitored variables.

Field Demonstrations of Thermally Enhanced Extraction

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Thermally Enhanced Extraction (TEE) is an innovative combination of groundwater extraction, soil vapor extraction, steam injection, hot air injection, and control techniques for accelerated and complete remediation. Results from two field demonstrations of TEE are described. The two TEE applications were removal of a dense nonaqueous phase liquid (DNAPL) pooled atop an aquitard in the saturated zone and stripping of volatile compounds from a residual hydrocarbon NAPL in a smear zone across the water table.

The DNAPL site contains two former trenches used to dispose of residuals from a solvent recovery unit. The disposed liquids seeped through the uppermost aquifer and accumulated in a geologic channel forming a pool in the saturated zone about 50 feet below the surface. The DNAPL consists of over 70% trichloroethene. Prior to the TEE demonstration, roughly 26,200 gallons of DNAPL had been recovered with a pump-and-treat system.

The TEE process included eleven days of thermal injection followed by twelve days of ambient air injection. Groundwater extraction and soil vapor extraction were performed during all phases. A bank of DNAPL preceded the thermal front and began to appear in extraction wells after one day of injection. Thermal breakthrough occurred in the extraction wells after three days of injection. Over 500 gallons of DNAPL were recovered from the demonstration area during the first five days of TEE. The TEE process removed an estimated total of 908 gallons of DNAPL in a 3-week period.

The EPA Superfund Innovative Technology Evaluation Program collected and analyzed soil samples from 14 locations immediately after the demonstration. Post-demonstration analyses of 42 soil samples revealed the average contaminant concentrations in the channel soil were reduced by 96%. The soil preliminary remediation goals were met in all 23 samples collected from the gravel channel and 13 of 19 samples collected from the underlying sand lens. This brief period of TEE treatment reduced the average soil concentrations in the underlying aquitard over 50%. This demonstration was the first field application of steam injection to remediate DNAPL in the saturated zone.

A second demonstration sponsored by the Strategic Environmental Research and Development Program (SERDP) was performed to increase understanding of steam injection and evaluate its effectiveness for cleanup of hydrocarbon NAPL. The field test was performed in a 10-by-15-foot cell enclosed by steel sheet-pile walls extending into a low permeability clay layer 30 feet below ground surface. Constituents of the NAPL were primarily weathered fuels and oils and chlorinated solvents.

Results of the steam injection test revealed very effective distillation of volatile contaminants from the residual NAPL. Compounds of concern showed reductions in soil concentrations greater than 95% in steam-swept layers. The final groundwater concentrations in the test cell were close to cleanup levels with only two target compounds exceeding the drinking water standard. As predicted by theory, the bulk NAPL was not effectively mobilized by the steam because of its high viscosity and low residual saturation; yet the low residual saturation allowed good contact between the steam and NAPL for distillation. Extracted vapor concentrations were well below saturated values for the elevated temperature suggesting the presence of water in the system inhibited distillation.

In Situ DNAPL Remediation Using Six-Phase Heating™

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The *in situ* cleanup of dense nonaqueous phase liquids (DNAPL) remains one of the remediation industry's toughest challenges. Standard remediation technologies require years of continued application to produce even marginal results. A new technology, Six-Phase Heatingä (SPH), has successfully remediated DNAPLs in demonstrations for the Environics Directorate of the US Air Force at the Dover AFB and for the Army Corps of Engineers at Fort Richardson. SPH has now been successfully implemented in full-scale remediations at several commercial and DOD sites including a recently completed large DNAPL site that is ready for site closure.

SPH is a polyphase electrical technology that uses *in situ* electrical resistive heating and steam stripping to achieve subsurface remediation. Developed by Battelle Memorial Institute at the Pacific Northwest National Laboratories (PNNL) for the US Department of Energy to enhance the removal of volatile contaminants from low-permeability soils, SPH has subsequently proven capable of remediating DNAPLs from saturated zones. SPH is now commercially available through Current Environmental Solutions (CES).

SPH transformers convert regular three-phase electricity into six separate phases. These electrical phases are then delivered throughout the treatment volume by steel pipe electrodes that are inserted using standard drilling techniques. SPH can quickly increase subsurface temperatures to the boiling point of water and is equally effective in all soil types, including fractured rock, under both vadose and saturated conditions.

The technology was originally developed for the treatment of low permeability soils. Since the original technology development, the treatment applications have been significantly expanded. SPH is now commercially available for the following treatment applications:

- Low permeability soils
- DNAPL and LNAPL Remediation
- Cold Regions Treatment
- Heavy Hydrocarbon Mobilization
- Rapid Clean Up
- Enhanced Biological Remediation
- Aquifer Heating

This presentation will also cover two case studies of the application of the SPH technology. The first case study will cover the successful remediation of a DNAPL plume under a former manufacturing building.

The second case study will cover the implementation of the SPH technology for the rapid remediation of a site with a pending property transfer. The site was a former dry cleaner and was contaminated with PCE and daughter products. The site was cleaned up to MCLs in 90 days of SPH operations.

RF Heating Technology for Soil Remediation

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Results from two sites, Ft. Wainwright, Alaska and an active retail petroleum facility in the Midwest demonstrate two applications of radio frequency (RF) antenna heating for safely accelerating site closures. At Ft. Wainwright located in a cold climate, preliminary results suggest that RF enhanced bioremediation during one year of an ongoing pilot test. The combination of RF with soil vapor extraction (SVE) at a Midwest United States retail petroleum facility and convenience store resulted in a six-month instead of a two to three year cleanup using only SVE.

Introduction

Remediation of soil and groundwater by established technologies is often costly and lengthy. RF heating applied by antennas offers a safe, cost-effective complement for a wide variety of remedial technologies. RF has application for accelerating remediation at sites contaminated with a variety of volatile and semi-volatile compounds. The RF heating process is not limited to 100°C temperatures.

RF heating for soil remediation by antenna technology brings controlled heating to the subsurface, increasing the rate of removal of contaminants from the soil. The antenna delivery system permits RF energy to be safely focused where needed, steered and directed (employing the interactions of multiple antennas), and delivered at the required depth. The antenna applicators may also be deployed with flexibility because casings can be oriented vertically, horizontally, or on an angle. RF delivered via antenna applicators is inherently safe because any high voltage points are shielded by the transmission line, soil, metal ground plane (if necessary), or the RF generating equipment. Periodic monitoring permits unrestricted site access by ensuring that above ground electromagnetic field levels are below OSHA (Occupational Safety and Health Administration) levels. Operation is at one of the ISM (Industrial, Scientific, and Medicine) frequencies allotted by the FCC (Federal Communications Commission). RF of course does not remove contaminants; it is a complement to other remedial technologies that increases their removal rates. Heating causes changes in the physical, chemical, and biological properties of soils, groundwater, and contaminants, making them more amenable to remediation efforts, thereby reducing remedial time frames and costs. RF has been applied with SVE, groundwater aeration (air sparging), product recovery, and bioremediation.

Two uses of RF are reviewed: the RF enhanced bioremediation pilot test at Ft. Wainwright, AK and the commercial cleanup in the Midwest United States at an active retail petroleum facility.

RF Heating Pilot Test at Fort Wainwright, Alaska

Cold soil temperatures limit the achievable biodegradation and volatilization rates of contaminants in soils in Alaska's interior. RF energy is being used at Ft. Wainwright to enhance two remedial technologies: bioremediation through bioventing and SVE during an extended pilot test of over a year in duration.

The pilot test is being conducted near the former fuel pump islands, where high concentrations of gasoline and diesel range organic compounds were measured from about 3 m below surface to several feet below the water table. Thus far, bioventing has been implemented for over a year, in which, a 12.2-m by 12.2-m by 3-m thick volume of soil was heated and maintained at a target temperature range of between 15°C and 35°C. An identical unheated (control) target area is located about 36.6 m from the RF heated area for comparison and analyses purposes. The ambient temperature of these soils is less than 6°C during the entire year.

The commercial RF heating system designed and deployed for heating the vadose zone consists of four independent 2.4-kilowatt (kW) continuous wave solid-state RF generators. The generators operate at 27.12 MHz. Each RF generator supplies energy via 2.2-cm transmission line to a 3-m long, 8.9-cm diameter antenna. The antennas are located in 15.7-cm diameter vertical fiberglass casings. The four antennas are separated by 6.1-m, deployed

in a square formation at wells RF#1, RF#2, RF#3, and RF#4, and are centered in the vadose zone at 3.3 m BG.

Preliminary results from the ongoing pilot test at a Fort Wainwright source area suggest that biodegradation rates can be improved substantially by RF heating. From May 19, 1998, the beginning of focused vadose zone heating, through March 11, 1999, 4,439 kWh were supplied by the RF heating system to raise the source area to the target temperature range of 15°C to 35°C. After heating the soils an additional 35,453 additional kilowatt-hours were required to maintain the within the target temperature range. The input of this RF energy has resulted in optimal soil temperatures for bioremediation. Biodegradation rates observed between the RF heated and unheated control areas increased by a factor of 6.

The RF system has operated remotely and essentially unattended since system startup and debugging. The biophase of the pilot test is ongoing and will evaluate the effect of adding nutrients to the soil on the biodegradation rate starting this summer. Column studies conducted at the University of Alaska in Anchorage on site soil suggest that biodegradation rates increase substantially when nutrients are added to RF heated soil. Following the biophase an 2-month long SVE phase will commence where the soils will be heated and maintained at 70°C to 90°C. When the pilot test is complete, a value engineering analysis will determine the potential for enhanced biodegradation and SVE as cost-effective remediation strategies at the site.

Commercial Application of RF Enhanced SVE at a Retail Petroleum Facility

An active Midwestern United States retail petroleum facility and convenience store is a site where RF antenna heating technology was applied to enhance SVE and achieve closure in substantially less time than conventional SVE. Contamination at this site was due to leaking underground storage tanks, pumps, and pipes and because of this, a dissolved phase plume was located approximately 9 m below grade. The site soils are glacial deposits consisting of coarse sands. In six months, from January through June of 1998, Dahl & Associates, a commercial licensee of KAI's RF heating technology accomplished what normally would have taken two to three years to achieve at ambient soil temperatures; site closure.

The RF system consisted of a trailer mounted computer controlled remotely operated 10-kilowatt 27.12 MHz RF generator and a 3 m long antenna applicator. The applicator was designed to heat vadose or capillary zone soils, but it was also used to heat the capillary zone by adjusting its length. Two at grade vertical wells were used to deploy the antenna applicator. The antenna applicator was raised and lowered in the wells so that it could focus RF energy into the capillary fringe or vadose zone during the course of the remediation. In addition to the RF wells there were seven air extraction wells and three air sparging wells at grade level. All transmission line and piping for the SVE and air sparging system were underground. A trailer mounted thermal oxidizer was used to destroy the organic compounds as they were extracted.

The successful cleanup of the retail petroleum facility marked the first commercial application of RF antenna heating with SVE and air sparging. During six months of operation the RF system raised soil temperature by approximately 30°C at 3 m from the RF wells and achieved temperatures in excess of 100°C at the RF wells. The SVE system during this same period recovered 2,305 kg (853 gallons) of gasoline range organics (GRO), an amount sufficient to achieve site closure. Based on its experience with similar sites in Minnesota, DAHL estimates it would normally take two to three years of SVE operation to close the site. This is over four times longer than when RF was applied with SVE. This result is also supported by the USEPA's Hyperventilate software which calculated a factor of four increase in the recovery rate of GRO when soil temperatures are maintained at an average 37.8°C (see Figure 1 below)
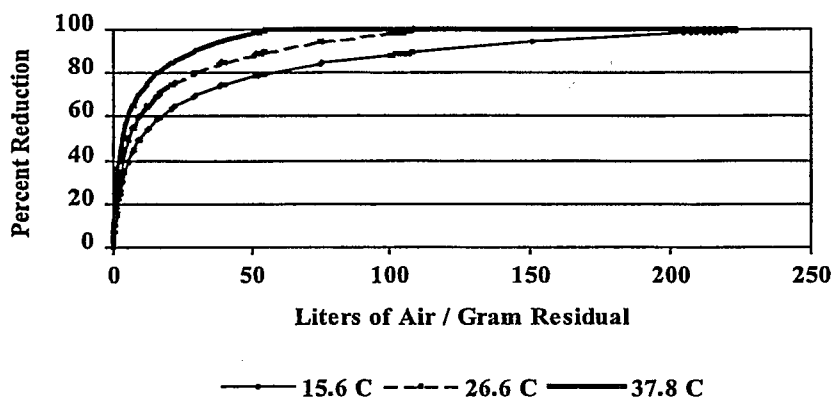
Figure 1. Hyperventilate calculations of GRO recovery.

Conclusion

KAI's RF antenna heating technology has been shown to significantly improve the performance of bioremediation and SVE thereby reducing time on site and the cost of remediation. Preliminary results from the ongoing pilot test and column studies at Ft. Wainwright, AK indicate biodegradation rate increases of two to ten fold are possible with the application of RF and the addition of nutrients. During its first commercial application, at a Midwest United States retail petroleum facility, RF antenna heating increased SVE off gas contaminant concentrations substantially and helped complete the cleanup of the site in six months instead of the usual two to three years required at ambient soil temperatures. RF antenna heating has another benefit an ability to co-exist safely with other site usage. This was most clearly demonstrated during the remediation of the retail petroleum facility and convenience store.

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Thermal Conduction Heating for *In Situ* Thermal Desorption

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In situ Thermal Desorption is a soil remediation process in which heat and vacuum are applied simultaneously to subsurface soils, either with surface heater blankets or with an array of vertical heater/vacuum wells. Near the high temperature (~900°C) heat sources, radiation heat transport dominates; however, at greater distances into the soil, thermal conduction accounts for the majority of heat flow.

As soil is heated, volatile contaminants in the soil are vaporized by a number of mechanisms, including: (1) evaporation into the air stream, (2) steam distillation into the water vapor stream, (3) boiling, (4) oxidation, and (5) pyrolysis. The vaporized water, contaminants, and natural organic compounds, are drawn by the vacuum in a countercurrent direction to the heat flow into the vacuum source at the blankets or wells.

Compared to fluid injection processes, conductive heat injection is very uniform in its vertical and horizontal movement. Furthermore, transport of the vaporized contaminants is improved by the creation of permeability, which results from drying and shrinking of the soil. Flow paths are created even in tight silt and clay layers, allowing escape and capture of the vaporized contaminants. The combined effectiveness of both heat and vapor flow yields nearly 100% sweep efficiency.

In addition, very high displacement efficiency (approaching 100%) can be reached in the heated soil. This occurs because the soil can be heated to high temperatures (>500°C) for prolonged times (many days). Field project experience has confirmed that a combination of high boiling temperature and long times result in extremely high overall removal efficiency of even the high boiling point contaminants from the soil.

In practice, most of the contaminants are destroyed in the soil before reaching the surface. Contaminants that have not been destroyed *in situ* are removed from the produced vapor stream at the surface with an air pollution control (APC) system.

In Situ Destruction of Chlorinated Hydrocarbon Compounds in a Reactive Well Using Pd-Catalysts

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Chlorinated solvents such as trichloroethylene (TCE), perchloroethylene (PCE), carbon tetrachloride, and chloroform are among the most commonly encountered groundwater contaminants. Conventional methods to remediate chlorinated solvent sites are expensive and thus there is a significant need for more cost-effective technologies. Many chlorinated hydrocarbon compounds are rapidly dechlorinated (within minutes) in the presence of dissolved H_2 and small quantities of Pd catalysts (Kovenklioglu, et al., 1992, Schreier and Reinhard, 1995; Siantar et al., 1996, Schüth and Reinhard, 1998, Lowry and Reinhard, 1999) without the production of intermediate transformation products often observed in biological systems. The rapid dechlorination rates permit the design of reactors that can be placed within the well bore of a treatment well for *in situ* groundwater remediation. This technology can be applied in aerobic aquifers, even though the process is reductive, because dechlorination of chlorinated ethylenes has been observed to be faster than the reduction of dissolved O_2.

Here we report on a prototype reactor for well bore treatment of chlorinated hydrocarbons that uses the H_2/Pd approach. The particular location at the LLNL site required a novel treatment approach because tritium co-contamination of the aquifer complicated the task of treating groundwater at the surface with conventional methods. The site is underlain by unconsolidated alluvial sediments, with the depth to groundwater approximately 30 m below the surface. The aerobic groundwater environment precluded natural reductive dehalogenation as a means of remediation, while the depth to groundwater rendered the placement of a permeable iron wall impractical. Given these constraints, the decision was made to test the remediation of the chlorinated hydrocarbons by an H_2/Pd reactor placed within a flow-through treatment well screened across two permeable sandy zones, separated by an aquitard. Both zones are characterized by similar contaminant chemical profiles: TCE, PCE, 1,1-DCE, chloroform, carbon tetrachloride, and 1,2-DCA, with a total contaminant concentration of 4 to 5 mg/L. Tritium was also present in both zones at a concentration of approximately 8,000 picocuries/L.

The reactor design is shown on Figure 1. Contaminated influent water is drawn into the well from the lower sand, hydrogenated, treated for chlorinated hydrocarbons by exposure to the Pd catalyst, and then discharged into the upper sand where tritium self-remediates through radioactive decay. The reactor has operated on a continuous basis for almost one year. The daily operating schedule has entailed 10 hours of operation, with flow reversal in the catalyst columns after 5 hours, followed by catalyst regeneration by flushing the reactor with aerobic water and subsequent overnight aeration.

Performance data, which have remained essentially constant over the operating history, are summarized on Table 1. Average contaminant removal is better than 98% except for chloroform (91%) and 1,2-DCA. The inability of the process to remove 1,2-DCA was as expected based on laboratory results (Lowry and Reinhard, 1999). Cost estimates suggest that a one year catalyst life-time is needed for the H_2/Pd technology to be competitive with granulated activated carbon (GAC) adsorption, not considering intangible benefits such as a small footprint and *in situ* destruction.

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Table 1. Ranges of contaminant concentrations (mg/L) measured at sampling points within the treatment system.

Compound	Influent	1st Catalyst column effluent	2nd Catalyst column effluent	System removal efficiency
TCE	3612-3777	<0.4-0.9	<0.4-0.8	>99%
PCE	366-370	<0.4	<0.4	>99%
Chloroform	167-235	11-38	6.5-36	~91%
1,1-DCE	130-180	<0.4	<0.4	>99%
1,2-DCA	26-28	20-26	19-27	~0
Carbon tetrachloride	18-21	<0.4	<0.4	>98%
Cis-1,2-DCE	0.6-0.7	<0.4-1	<0.4-0.9	-
Vinyl chloride	<0.4	<0.4	<0.4	-

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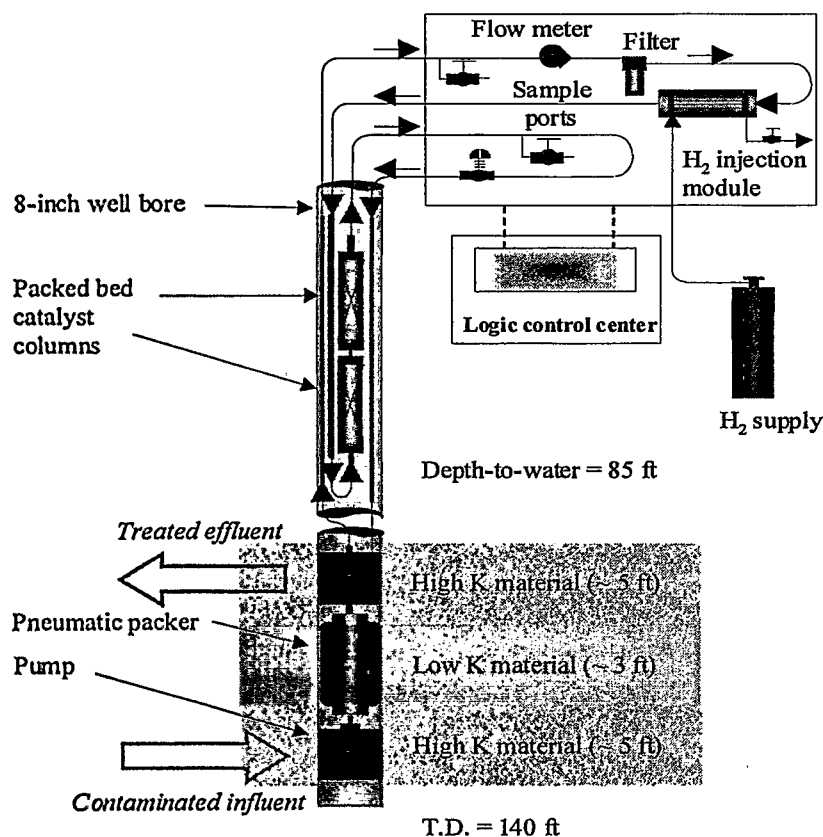
Acknowledgments

Figure 1. H_2/Pd Reactor

Case Studies of *In Situ* Chemical Oxidation using the Geo-Cleanse® Process

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Introduction

The Geo-Cleanse Process is a patented, *in situ* chemical oxidation technology to deliver hydrogen peroxide and ferrous iron catalyst (Fenton's reagent) to the subsurface. The Geo-Cleanse Process is a pressurized system capable of oxidizing many organic contaminants in both soil and groundwater. The Geo-Cleanse Process has in the past six years been applied at over 50 sites in 17 states and in Canada, to address common organic contaminants ranging from petroleum hydrocarbons (BTEX), chlorinated solvents (PCE and TCE) including DNAPLs, nitroaromatic compounds (RDX, TNT, DNT), and manufactured gas plant PAH contamination. Cleanup objectives as low as non-detectable levels (<1 mg/L) in groundwater.

The purpose of this presentation is to briefly review several recent case studies of Geo-Cleanse Process applications at several Department of Defense and private industrial facilities. Seven sites, all treated within the past year, are described. Four of the seven sites are impacted by chlorinated aliphatic solvents (e.g., PCE), one is impacted by chlorinatedaromatic solvents (trichlorobenzene), one is impacted by jet fuel, and one is a former manufactured gas plant impacted by extremely high levels of polycyclic aromatic hydrocarbons (PAHs). These case studies represent a wide range of geological and hydrogeological conditions and a variety of organic contaminants. Two of the sites are currently in treatment, and thus only the pre-treatment site conditions and the work plan are summarized.

Kings Bay Naval Submarine Base, Georgia

PCE and its natural degradation products (TCE, cis-1,2-DCE, vinyl chloride) were detected in groundwater underlying the Old Camden County Landfill, now located within the boundaries of Kings Bay Naval Submarine Base. The groundwater plume was migrating off base towards an adjacent residential neighborhood. The maximum groundwater VOC concentration was 9,074 mg/L of total chlorinated aliphatic hydrocarbons (sum of PCE, TCE, cis-1,2-DCE, and vinyl chloride concentrations), primarily PCE (8,500 mg/L). The PCE concentration exceeded 1% of the water solubility, implying the presence of a residual DNAPL phase of unknown mass. The treatment goal was to achieve a total chlorinated aliphatic hydrocarbon concentration of <100 mg/L, a level considered sufficient to allow natural attenuation to reduce VOCs to MCLs to prevent migration of the plume beyond base boundaries. The site geology is characterized as medium to fine sands, and the targeted treatment zone was an interval of relatively high conductivity located from approximately 30 to 40 ft below grade. An oval-shaped source area approximately 120 ft long x 40 ft wide was targeted for treatment.

A full-scale Geo-Cleanse Treatment was conducted at the site in cooperation with Bechtel Environmental, Inc. and the Naval Facilities Engineering Command, Southern Division. A total of 23 specially designed injectors were installed in an array encompassing the target treatment area. A total of 12,045 gallons of 50% hydrogen peroxide was injected in 26 days during two treatment phases in November 1998 and February 1999. Groundwater samples were collected before, during and after treatment. The remedial objective of <100 mg/L was achieved within the treatment area following the first treatment phase. The second treatment phase targeted the area primarily downgradient of the primary treatment area, in order to achieve further reductions. The results indicate destruction of >99% of the dissolved chlorinated aliphatic hydrocarbons in groundwater, with a reduction to 9 mg/L from 9,074 mg/L within the primary source area. All monitoring wells within or adjacent to the treatment area achieved the cleanup objective of <100 mg/L and have maintained compliance to date (up to 9 months after treatment). In addition, monitoring wells and recovery wells located downgradient also exhibited significant reductions.

As a result of the Geo-Cleanse Treatment Program, the Navy was recognized and given an award for environmental awareness by the State of Georgia Department of Natural Resources, and a long-term pump-and-treat system to control plume migration was removed from service. Based upon these very positive results, the scope of work was expanded in June 1999 to include additional downgradient and upgradient source areas in order to achieve even greater reductions outside of the initial treatment area. The additional treatment was conducted in June and July 1999. Preliminary data indicate further reductions and successful treatment of the expanded area.

Pensacola Naval Air Station, Florida

TCE and its natural degradation products (cis-1,2-DCE and vinyl chloride) and aromatic hydrocarbons (primarily chlorobenzene isomers) were detected in a groundwater plume originating under a former sludge drying bed at the Industrial Wastewater Treatment Plant at Pensacola Naval Air Station. Site characterization data delineated a groundwater plume migrating northeast towards Pensacola Bay. The cleanup goal was to eliminate source area contamination in order to enhance natural attenuation of the downgradient plume and thereby prevent subsurface discharge to Pensacola Bay. The maximum concentration of total VOCs dissolved in groundwater was 4,896 mg/L, composed primarily of TCE (3,600 mg/L). The site geology is characterized as medium to fine sands with groundwater at approximately 4 ft below grade. The primary targeted treatment zone was an interval of relatively high conductivity located from approximately 35 to 45 ft below grade.

A full-scale Geo-Cleanse Treatment was conducted at the site in cooperation with the Naval Facilities Engineering Command, Southern Division and the Naval Facilities Engineering Service Center. A total of 15 specially designed injectors were installed in an array encompassing the target treatment area. Six of the injectors were installed at shallower depths within the source area to target contamination at the suspected source. The remaining nine injectors were installed within the 35 to 45 ft depth interval.

A total of 10,160 gallons of 50% hydrogen peroxide was injected in 13 days during two treatment phases in December 1998 and in May 1999. Groundwater samples were collected before, during and after each treatment. The results indicate destruction of >96% of the dissolved chlorinated aliphatic hydrocarbons in groundwater, with a reduction of total VOCs to non-detect (<1 mg/L) from 4,896 mg/L in the most contaminated monitoring well. These reductions have been maintained in all compliance points to date (from a sampling round conducted 30 days following injection).

Fort Dix 4400 Area Spill Site, New Jersey

Fort Dix is located in the Pine Barrens region of central New Jersey, considered an environmentally sensitive re-

gion because it is the recharge area for the Kirkwood-Cohansey Aquifer, the primary source for domestic wells in the area. The shallow aquifer at the site is characterized as medium to fine sand extending to a depth of approximately 40 ft below grade. Motor pool operations at the Fort Dix facility resulted in a discharge of chlorinated solvents to the shallow groundwater. The maximum historical concentration of total VOCs was 132 mg/L, primarily PCE (65 mg/L). The maximum concentration immediately prior to treatment was 24.6 mg/L, primarily PCE (11.2 mg/L). Due to the environmental sensitivity of the site, an extremely rapid and effective solution was desired, with a cleanup objective of 1 mg/L.

A full-scale Geo-Cleanse Treatment Program was conducted at the site in cooperation with ICF Kaiser Engineers, Inc. (now part of the IT Group). Twenty-four specially designed injectors were installed in two discrete levels at the site to encompass the vertical and horizontal distribution of contaminants. A total of 5,708 gallons of 50% hydrogen peroxide was injected over the course of a 7-day field treatment program in February 1999. The results indicate that the maximum dissolved concentration of total VOCs was reduced to 1.0 mg/L from 24.6 mg/L (96%), thus achieving the remedial goal. These levels were maintained for a groundwater sampling event 14 days following treatment, and additional quarterly monitoring is planned.

Fort Stewart, Georgia

Fueling operations resulted in jet fuel contamination of soil and groundwater at Wright Army Airfield, Fort Stewart, Georgia. The geology of the site is marked by a distinctive stiff clay- and silt-rich sand interbedded with red and grey mottled clay layers, interpreted as an ancient soil (paleosol) weathering horizon. The paleosol is underlain by fine to medium quartz sand extending at least 25 ft below grade. Soil investigations identified two distinct layers of contamination, at approximately 13 and 17 ft below grade, indicated by stained soils, petroleum odors, and globules of free product floating on water samples. Soil sampling indicated maximum total petroleum hydrocarbon contamination of 906 mg/kg, and maximum dissolved concentrations of fuel components (sum of BTEX, 2-methylnaphthalene, and naphthalene) of 7,331 mg/L.

A Geo-Cleanse Pilot Treatment was conducted in collaboration with Science Applications International Corporation (SAIC) and the Fort Stewart Directorate of Public Works, Environmental Branch, to demonstrate effectiveness of the Geo-Cleanse Process on jet fuel at the Fort Stewart site. Six specially designed injectors were installed surrounding a monitoring well. Four of the injectors targeted the shallower contaminated interval (13 ft below grade) and two injectors targeted the deeper zone (17 ft below grade). A total of 2,537 gallons of 50% hydrogen peroxide was injected over a five-day period in September 1998.

Because the pre- and post-injection soil sampling locations do not correspond exactly, the site was partitioned

into two areas. Pre-injection soil results for Area 1 ranged from 1.4 mg/kg to 906 mg/kg, and one post-injection sample yielded 4.9 mg/kg. Pre-injection soil results for Area 2 ranged from 65.8 mg/kg to 837 mg/kg, and one post-injection sample yielded 779 mg/kg. Groundwater samples also indicate significant reductions in dissolved fuel components (sum of BTEX, 2-methylnaphthalene, and naphthalene). The central monitoring well exhibited a reduction to 80 mg/L from 839 mg/L (90% destruction). On a site-wide average comparing three pre- and post-treatment samples, dissolved fuel components were reduced to 906 mg/L from 4,051 mg/L (78% destruction). The objective of demonstrating effectiveness of the Geo-Cleanse Process on jet fuel contamination at the Fort Stewart site, in a very heterogeneous, dense, clay-rich paleosol horizon, was successfully achieved.

Former Industrial Site, Ohio

Operations at this former industrial site used trichlorobenzene as a solvent during synthesis of an organic chemical product. A DNAPL phase composed primarily of 1,2,4-trichlorobenzene was identified in a sand and gravel aquifer. The DNAPL collected in discrete pools on an underlying stiff clay layer, under the razed building foundation, at a depth of approximately 20 to 22 feet below grade. One pool was targeted for a pilot treatment with the Geo-Cleanse Process. The volume of DNAPL present was difficult to estimate, but as much as 4.5 feet of DNAPL accumulated in a recovery well within the treatment area. Other organic contaminants reported at the site included other isomers of trichlorobenzene, isomers of dichlorobenzene, naphthalene and bis(2-ethylhexyl)phthalate. Additionally, ammonia was reported at levels up to 590 mg/L within the treatment area. Ammonia is a highly basic compound that is not effectively destroyed by Fenton's reagent.

Groundwater at the site was found to have a pH of 7.2 to 8.2, with some samples yielding a pH as high as 11. The ammonia and very basic groundwater pH presented challenges because of the buffering capacity of the groundwater (Fenton's reagent is most effective at mildly acidic groundwater pH conditions) and radical trapping properties of the non-targeted compounds.

The goal of the Geo-Cleanse Pilot Treatment were to reduce DNAPL mass within the targeted treatment area to demonstrate effectiveness of the Geo-Cleanse Treatment Program at the site. Six specially designed injectors and two specially designed vent wells were installed within the treatment area. The vent wells were installed with screens extending into the vadose zone soil and a blower pump was attached, in order to draw any ammonia vapors that might be entrained with gases (oxygen and carbon dioxide) resulting from the Geo-Cleanse Process. The pump effluent was passed through a water trap and carbon filter to capture any ammonia vapors. A total of 3,016 gallons of 50% hydrogen peroxide solution was injected over the course of five days in August 1998.

Dissolved 1,2,4-trichlorobenzene levels decreased overall across the site as a result of the Geo-Cleanse Pilot Treatment. The volume of DNAPL within the treatment area was reduced dramatically. DNAPL was eliminated during the treatment in three monitoring wells that previously accumulated DNAPL, including PMW-14 (formerly 3.78 feet collected), PMW-1 (formerly 0.04 feet collected) and PRW-3 (formerly 1.60 feet collected). Two other monitoring wells located adjacent to the treatment area experienced reductions in dissolved 1,2,4-trichlorobenzene levels and no change in DNAPL accumulation thickness. An additional observation was that, after treatment, only the wells installed into the underlying clay accumulated DNAPL, suggesting that the residual DNAPL remaining after treatment was confined to the upper portion of the underlying clay layer rather than in the targeted sand and gravel interval.

Letterkenney Army Depot (DA Area Bedrock), Pennsylvania

Letterkenney Army Depot was established as an ammunition storage facility in 1942, with additional missions including overhaul and maintenance of wheeled and tracked vehicles, issue and shipment of chemicals, maintenance of missile systems, and ammunition maintenance and demilitarization. Operations resulted in disposal of industrial solvents and other wastes within the Disposal Area (DA), and the DA was placed on the National Priorities List in July 1987. A Geo-Cleanse Pilot Treatment was conducted within the DA in order to evaluate effectiveness of the Geo-Cleanse Process within a limestone bedrock formation. This application was innovative because of the relatively high alkalinity and pH of the groundwater and expected reactivity of the native limestone bedrock at the site towards acidic reagents utilized during the Geo-Cleanse Process. Contaminated areas in the unconsolidated soil overburden was excavated in 1993-94. However, groundwater contamination within the underlying fractured bedrock aquifer was not addressed. The bedrock aquifer at the site was the subject of intensive investigation supported by the U.S. Army Corps of Engineers. Total VOC concentrations in groundwater ranged from 18 to as high as 3,000,000 mg/L, with TCE and its natural degradation product cis-1,2-DCE as the primary contaminants present within the pilot treatment area.

A Geo-Cleanse Pilot Treatment was conducted at the site in collaboration with Roy F. Weston, Inc. and the U.S. Army Corps of Engineers. A total of 12,635 gallons of hydrogen peroxide were injected over 4 days in June 1999. Final analytical results are not yet available. However, field parameters indicate a successful treatment. The bedrock aquifer was able to sustain very high overall injection rates, resulting in an expected very wide radius of influence. Groundwater samples for VOC analysis have not yet been collected. However, hydrogen peroxide is persistent in the monitoring wells and injectors within the area 25 days after completing the injection.

Former Manufactured Gas Plant, Wisconsin

The site of a former manufactured gas plant in southeastern Wisconsin is slated for redevelopment by the year 2001. Redevelopment cannot be completed until remaining groundwater and saturated soil contamination is remediated. Unsaturated soils at the site were excavated in 1995, but residual contamination within the saturated zone remains very high. BTEX and PAH compounds are the primary contaminants present, with concentrations as high as 59,288 mg/kg of BTEX and 404,060 mg/kg of PAH sorbed to saturated zone soils within the targeted pilot treatment area. Groundwater is at approximately 5 ft below grade and limestone bedrock is encountered at approximately 15 ft below grade. The soils within the saturated zone are generally described as silty sand and gravel with some cobbles.

Bench-scale testing indicated that the Geo-Cleanse Process can effectively oxidize the PAH and BTEX compounds present in the soil at the site. Accordingly, a Geo-Cleanse Pilot Treatment was conducted to determine if the Geo-Cleanse Process offers a viable remedial alternative. Approximately 7,200 gallons of 50% hydrogen peroxide solution were injected in 11 days in July 1999. Final analytical data are not yet available. However, field indications, primarily carbon dioxide production as a result of hydrocarbon oxidation, indicate a very efficient chemical oxidation reaction.

Summary

While no treatment technology is appropriate for every site, *in situ* chemical oxidation can provide a viable technology to achieve cleanup objectives in a cost-effective and timely manner. Case studies are presented in this summary for seven sites treated by the Geo-Cleanse Process. The contaminants at the sites include chlorinated solvents, polycyclic aromatic hydrocarbons, and aromatic hydrocarbons, in a wide range of geological and hydrogeological settings. The case studies demonstrate that the Geo-Cleanse Process is a robust technology for *in situ* chemical oxidation that is applicable to a wide variety of contaminants and site conditions.

Interagency DNAPL Consortium

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Federal agencies have been using shrinking environmental research and development resources to address environmental contamination caused by dense non-aqueous phase liquids. When technologies do appear promising, there is a lengthy period before they are accepted by site owners, stakeholders, and the regulatory community. Usually, there is no direct comparison between technologies to determine cost and performance data.

In an attempt to better use our resources, and address the DNAPL problem, several agencies have joined forces. The Interagency DNAPL Consortium is working together at Cape Canaveral Air Station, Florida to demonstrate three promising DNAPL source remediation technologies. We feel there are several benefits to this partnership.

Benefits

- Multi-agency cooperation
- Cost shared demonstrations
- Side-by-side, real-time technology demonstrations
- Accelerated technology deployment
- Share/develop expertise among agencies with common problems
- Comparative cost-data for technologies
- Shared agency solutions for common problems

Problems

Dense Non-Aqueous Phase Liquids (DNAPLs) pose serious, long-term groundwater contamination problems due to their toxicity; limited solubility in groundwater; and significant migration potential in soil gas, groundwater, and/ or as separate phase liquids. DNAPL chemicals, particularly chlorinated solvents, are among the most common of environmental contamination problems in the United States as well as for most industrialized countries. There are thousands of DNAPL-contaminated sites in the United States, often at contaminant volumes that are difficult to detect, but in quantities that can represent significant sources of groundwater contamination. Many agency and private-sector sites have DNAPL contamination problems, including federal, state and local government agencies. The Office of Management and Budget estimates that the federal government alone will spend billions of dollars for environmental clean-up of DNAPL contamination problems.

While various DNAPL remediation, characterization and monitoring technologies have been demonstrated in the past, it is difficult, if not impossible, to make meaningful comparisons of either performance or cost among these technologies because of the variable conditions at the demonstration sites. As a result, "problem holders" and regulatory officials have been reluctant to deploy these technologies for site clean up. In order to expedite the regulatory acceptance and use of these innovative remedial technologies, comparative cost and performance data must be collected.

Solutions

An important step in reducing technology risk and increasing user and regulatory acceptance of DNAPL remediation, characterization and monitoring technologies involves conducting concurrent, "side-by-side" field demonstrations. These side-by-side demonstrations result in comparative cost and performance data collected under the same field conditions. Through appropriate documentation, the resulting cost and performance data can be evaluated for site-specific applications. Side-by-side demonstrations help to fill an important "gap" in the process of technology development and deployment and will accelerate technology privatization.

In 1998, a multiagency consortium was organized by the United States Department of Energy/Office of Environmental Management (DOE/EM) and the Department of Defense (DOD) through the Air Force Research Laboratory (AFRL) in cooperation with the 45th Space Wing, the National Aeronautics and Space Administration (NASA) and the United States EPA (EPA) to demonstrate innovative DNAPL remediation and characterization technologies at a NASA remediation site on Cape Canaveral Air Station,

Cape Canaveral, FL. This Interagency DNAPL Consortium (IDC) was formed to:

- *address* a serious, widespread and shared environmental problem adversely affecting many U.S. federal agencies (e.g., DOE, EPA, DOD, NASA, Department of Interior, Department of Agriculture);

- cost-share the demonstration and comparison of these remediation and monitoring system technologies;

- *accelerate* both the demonstration and deployment of DNAPL remediation, characterization and monitoring technologies for the purpose of reducing the perceived technology risk associated with these technologies;

- *increase* regulatory and user acceptance of these technologies by providing documented, cost and performance data; and

- *provide* increased opportunities to test new sensors designed to support *in situ* remediation of DNAPL contamination problems in addition to *ex situ* treatment and disposal.

In order to conduct this side-by-side demonstration, an IDC Core Management Team was organized. The IDC consists of representatives from DOE, NASA, USAF, DOD and EPA. The Team is a collaborative decision-making body that draws upon the strengths of each agency to solve problems associated with the project. The Team utilizes a Technical Advisory Group (TAG) for support in making decisions that concern individual evaluation of remediation systems. The IDC TAG is comprised of experts from industry, academia and federal agencies. With the support of the TAG, the Team selected three of the most promising remediation technologies (Figures 1-3) for deployment and evaluation at Launch Complex 34. Florida State University's Institute for the Team for International Cooperative Environmental Research provides day to day field project management through a cooperative agreement with the Department of Energy.

Remediation Technologies

Thermal Treatment for Mass Removal - Electrical Resistance Heating

The Six Phase Soil Heating technology (Figure 1) removes contaminants from soil and groundwater by passing an electrical current through the soil matrix. The passage of current generates heat due to electrical resistance within the soil. This is the same process used in any electrically heated device (e.g., clothes iron, heater, stove). Heat is generated throughout the soil in the remediation area and the temperature of the soil is increased to the boiling point of water. Soil moisture becomes steam that is captured by vapor recovery wells for removal. Soil contaminants are vaporized concurrently and are captured for *ex situ* treatment.

Benefits

- Heat is generated uniformly throughout the treatment volume. While low permeability lenses reduce the performance of other technologies that rely on the vertical movement of a fluid or vapor though the soil matrix, soil heterogeneity or low permeability does not adversely effect Six Phase Soil Heating. In fact, low permeability soils tend to carry greater current than do sandy soils, thus, become hotter, and boil constituents faster.

- Anaerobic dechlorination of solvents will add conductive chloride ions to "hot spots", likewise attracting current for faster remediation of the impacted regions of the site.

- The boiling of soil moisture in clay lenses forms steam to "sweep out" volatile organic compounds. This steam stripping process effectively increases the permeability of clay soils.

- Because Six Phase Soil Heating treats all soils in the treatment volume, there are no untreated regions from which contaminants could diffuse later and cause rebound. Rebound has not been observed at any Six Phase Soil Heating site.

- The presence of perched water does not reduce the effectiveness of Six Phase Soil Heating.

In Situ Chemical Oxidation - Potassium Permanganata (KMnO$_4$)

In situ oxidation using potassium permanganate (Figure 2) is a potentially fast and low cost solution for the destruction of chlorinated ethylenes (TCE, PCE, etc), BTEX (benzene, toluene, ethylbenzene, and xylene) and simple polycyclic aromatic hydrocarbons. In particular, potassium permanganate reacts effectively with the double bonds in chlorinated ethylenes such as trichloroethylene, perchloroethylene, dichloroethylene isomers, and vinyl chloride. It is effective for the remediation of DNAPL, adsorbed phase and dissolved phase contaminants and produces innocuous breakdown products such as carbon dioxide, chloride ions and manganese dioxide. The permanganate solution typically is applied at concentrations of one to three percent solution via injection wells. This solution is easily handled, mixed and injected and is non-toxic and non-hazardous.

Bench scale laboratory tests of potassium permanganate with trichloroethylene have resulted in up to a 90% reduction of trichloroethylene in four hours of treatment. The effectiveness of the *in situ* injection of permanganate is a function of the reaction kinetics, the transport and contact between potassium permanganate and the contaminant, as well as competitive reactions with other oxidizable species (e.g., iron, natural organics). The effective use of this remedial technology requires an engineered approach for maximizing the contact between potassium permanganate and the target contaminant. As with many technologies, low permeability and heterogeneity of soils present a challenge and require a carefully designed application system.
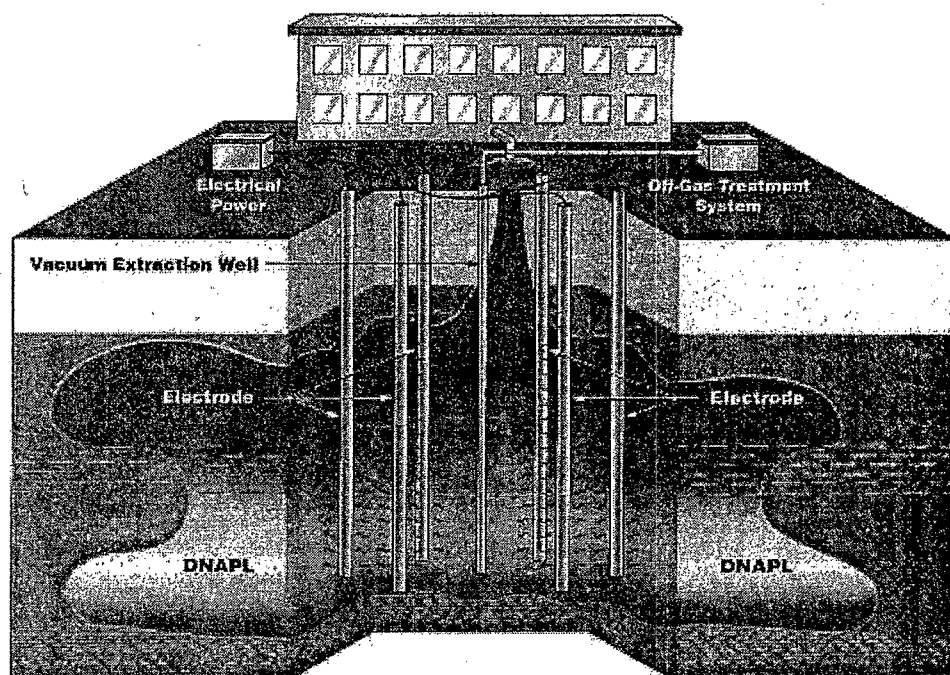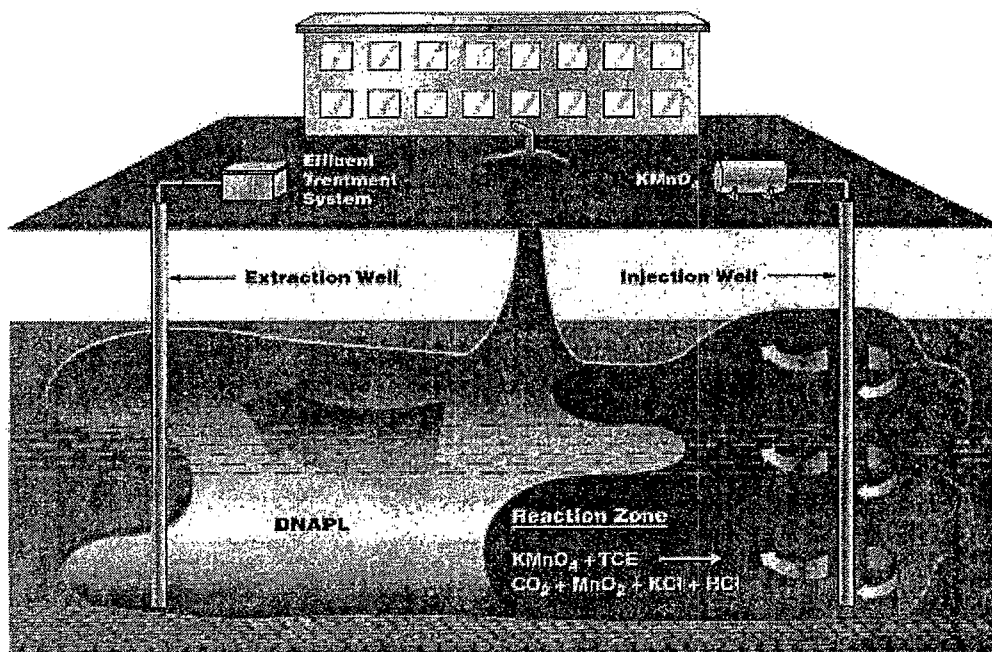
Figure 1. Six Phase Soil Heating.

Figure 2. In Situ Chemical Oxidation with Permanganate.

Benefits:

- Chemically oxidizes a wide range of organic compounds to innocuous end-products over a wide pH range

- Visible (purple) solution makes it easy to track the injection influence or the degree of treatment

- Chemically stable in water (very slow auto-degradation)—stays in solution until it is reacted

- No off-gas treatment required

Thermal Treatment for Mass Removal
Steam Stripping

Thermal remediation by steam injection and recovery uses Dynamic Underground Stripping, Steam Enhanced Extraction, Hydrous Pyrolysis/Oxidation, and Electrical Resistance Tomography. Combining these technologies the Dynamic Underground Stripping System uses boilers to generate steam which is then pumped into injection wells that surround the contaminants. The steam front volatilizes and mobilizes the contaminants as it pushes the resulting steam front toward a central network extraction well where it is vacuumed to the surface. Direct electrical heating of soils, clay and fine-grained sediments causes trapped water and contaminants to vaporize and forces them into steam zones where vacuum extraction removes them. Electrical Resistance Tomography is used as a process control method to measure electric resistance and temperatures in the subsurface that allow for real-time control of the heating process.

Benefits

- Faster clean-up, potential closure within months to years, not decades

- Removes source contaminants effectively

- Treats contamination both above and below the water table, with no practical depth limitation

Sensor Technology Evaluations

In addition to DNAPL remediation technology demonstrations, the project provides the opportunity to evaluate innovative characterization technologies for locating DNAPL, *in situ* lithologic mapping, *in situ* vadose zone and saturated zone sampling and *in situ* hydraulic conductivity measurements. These technologies were deployed using the DOE and EPA Site Characterization and Analysis Penetrometer System (SCAPS) trucks. In addition to sensor technology evaluation, the SCAPS trucks have been used for data collection essential to conceptual model design and strategic location of critical lithologic units, sediment sampling and monitoring well placement. The following cone penetrometer (CPT) based sensors and sampling tools have been deployed at the site:
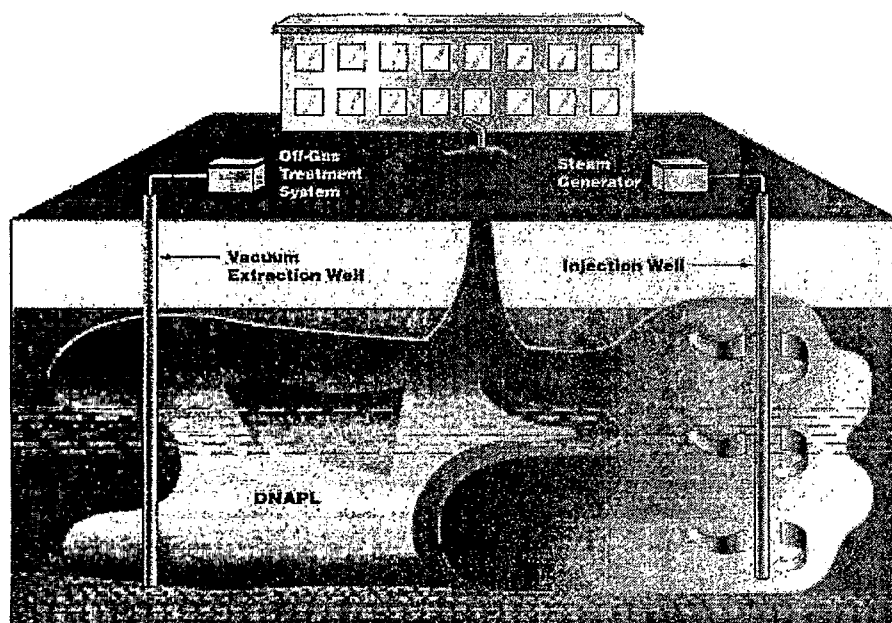

Figure 3. *In Situ* Thermal Remediation (Steam Injection)

- Raman spectroscopy: used for direct detection of DNAPL in the subsurface
- GeoVIS: soil video imaging system used for visual characterization of critical stratigraphic units and visual detection of DNAPL
- Cone Permeameter™: *in situ* permeability measurements
- Cone Sipper: multiple depth discrete soil gas and groundwater sampling
- FLUTE: Hydrophobic Flexible Membrane is a sampling device that can provide detailed delineation of DNAPL in a borehole
- Precision Injection/Extraction (PIX) Probe: characterization method for determining the presence or absence of depth discrete DNAPL

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Field Pilot Test of *In Situ* Chemical Oxidation Through Recirculation Using Vertical Wells at the Portsmouth Gaseous Diffusion Plant

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Introduction

In situ chemical oxidation is an emerging remediation technique in which chemical oxidants are delivered to the subsurface to rapidly degrade organic contaminants (Siegrist 1998, US EPA 1998). For the past 6 years, engineers and scientists at Oak Ridge National Laboratory (ORNL) have been developing this technology for *in situ* degradation of organic chemicals such as trichloroethene (TCE), perchloroethene (PCE), naphthalene, and pyrene (Gates and Siegrist 1995; West et al. 1997); Siegrist et al. 1998a and 1998b). Laboratory-scale experiments performed to date have demonstrated that permanganate (MnO_4^-), if applied at sufficient loadings, can effectively oxidize TCE and PCE. The following describes the overall chemical reaction for the oxidation of TCE using potassium permanganate (eqn.1):

$$2KMnO_4 + C_2HCl_3 \rightarrow 2CO_2 + 2MnO_2 + 2KCl + HCl$$

Permanganate is commonly used in waste water treatment to oxidize organic compounds and is commercially available in two forms, $KMnO_4$ and $NaMnO_4$. While the behavior and oxidation potential of the two compounds is similar, the aqueous solubility of $NaMnO_4$ is much higher (~50% vs. ~6%). The relative stability of MnO_4^- makes it attractive as an *in situ* chemical oxidant since it can be delivered and dispersed in soil and groundwater and has the ability to migrate by diffusion into fine-grained zones where residual contaminants may exist.

To continue development of *in situ* chemical oxidation for widespread use and commercial viability, techniques for delivering chemical oxidants in adequate amounts to the subsurface are being developed (Case, 1998; DOE 1996a; Gates and Siegrist 1995; Lowe et al. 1998; Siegrist et al. 1994, 1995, 1998a, 1998b, 1999; Struse 1999; West et al. 1995). Initially, an *in situ* chemical oxidation through recirculation (ISCOR) treatability study was conducted at the U.S. Department of Energy Portsmouth Gaseous Diffusion Plant (PORTS), Piketon, Ohio, involving injection and recirculation of an oxidant solution (~2wt.% $KMnO_4$) through paired horizontal wells and selected vertical wells (West et al. 1997). Although oxidant delivery/recirculation was impacted by heterogeneity within the demonstration area, where the oxidant was able to permeate the aquifer, significant and sustained reductions in TCE were measured in soil and groundwater. The goal of this field pilot test was to test an alternative oxidant delivery approach using recirculation via vertical wells in a 5-spot pattern to develop a sufficient understanding of ISCOR to facilitate completion of the Corrective Measures Study process. The test design was comprised of a 5-spot vertical well pattern with the central well serving as the injection point (Figure 1).

The four corner extraction wells were placed in a square grid surrounding the injection point on a fixed radius of 45 ft. Several monitoring wells were also installed throughout the region to monitor changes in contaminant concentrations, oxidant concentrations, water quality parameters, and water levels during operation. The system was designed to accommodate recirculation flow rates of 2 to 20 gpm supplemented with $NaMnO_4$ to maintain delivery of the oxidant concentration at ~250 mg $NaMnO_4$ per L of re-injected groundwater.
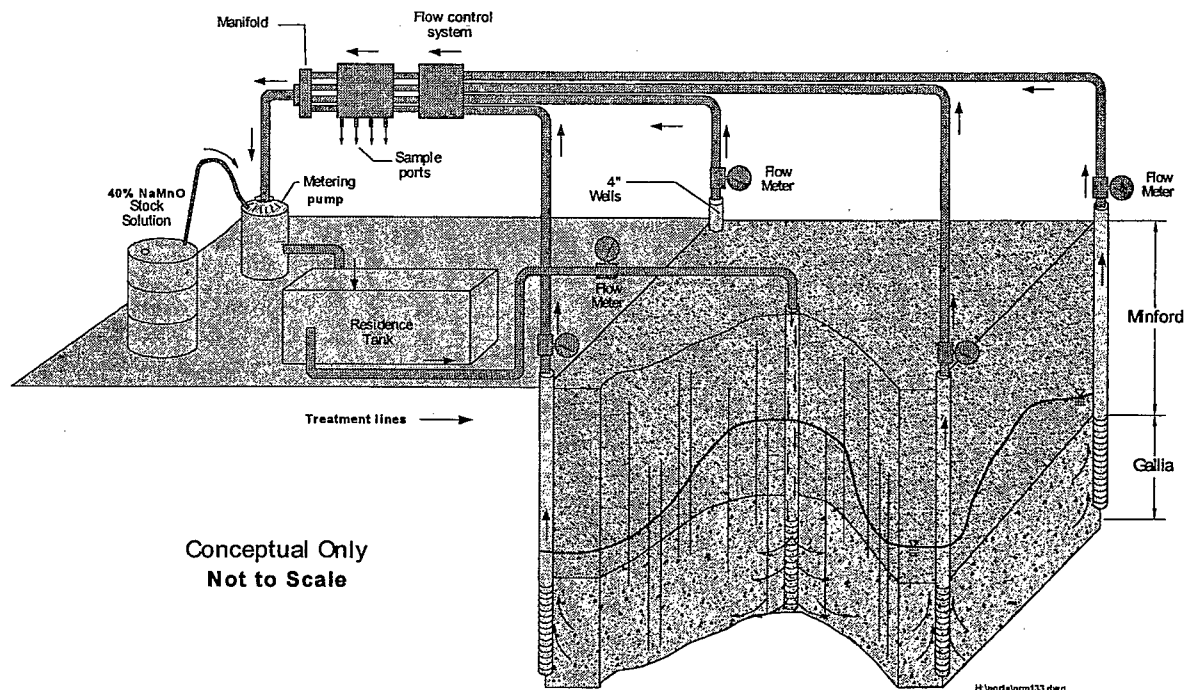
Figure 1. Conceptual diagram of vertical well injection/recirculation system.

The advantages of the use of liquid NaMnO$_4$ and a vertical well recirculation approach include: (1) better control of oxidant and contaminant migration within the treatment zone when compared to single well injections, (2) the introduction of higher volumes of oxidant solutions in a given time because existing soil pore water is extracted concurrent to oxidant injection, (3) easier oxidant handling, and (4) potentially lower overall cost for treating larger volumes.

Methods

The field pilot test was conducted within the source area of the 5-Unit Investigative Area, immediately south of the X-770 Building, at PORTS. The geology under the pilot test cell area is comprised of 23-26 ft of Minford sediments underlain by 3 to 8 ft of Gallia. Both units are unconsolidated, Quaternary age members of the Teays formation. The Gallia lithology is typically comprised of a saturated silty-sandy gravel unit of higher permeability overlying a drier lithified unit of coarse angular gravel in a silty clay matrix. The upper more permeable member of the Gallia varies in thickness from 0.5 to 2.5 ft. The Gallia is thicker and more permeable across the southern two thirds of the test cell area. In general, 5-Unit Area groundwater flows horizontally from north to south and the hydraulic gradient is very low (0.001) because of the flat valley floor, the presence of thicker and more permeable Gallia deposits, and the proximity of the east-west-trending groundwater divide present along the central part of the facility.

The field pilot test required the installation, development, and hydraulic testing of wells, baseline soil and ground-water characterization, and assembly of the oxidant delivery system. One 6-in diameter injection well, four 4-in diameter extraction wells and nine 2-in diameter monitoring wells to monitor the pilot test operations were installed (Figure 2). Soil and groundwater characteristics, physical and chemical, were obtained throughout the area prior to recirculation. Hydraulic tests (pressure injection test and single well tests) were performed to select the recirculation pumping and injection rate and to determine the distribution of permeability within the test area.

A conservative tracer (bromide) was added at the initiation of injection/recirculation to enable detection of the injected water within the treatment area. Approximately 500 gals of 1800 mg/L bromide solution were injected at 18 gpm into the central injection well with equal extraction (4.5 gal/min) at the four corner extraction wells. Concurrently, groundwater samples were collected from each monitoring location and extraction well and analyzed for bromide using an ion selective electrode at 15 to 30 minute intervals until movement of the bromide past the monitoring location was detected. This information was used to determine preferential flow paths, to measure the extent of hydraulic control in the treatment area, and to define the rate and extent of anticipated NaMnO$_4$ transport.

The oxidant delivery system was assembled along the northern side of the test cell. The major components of the system comprise flow and pressure control, oxidant dosing and delivery, and sample ports. System flow rates, pressures, water levels, oxidant feed concentrations, movement/reaction of the oxidant through the Gallia aquifer

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Legend:

- ○ Existing Extraction Well
- ▼ Existing Monitoring Well
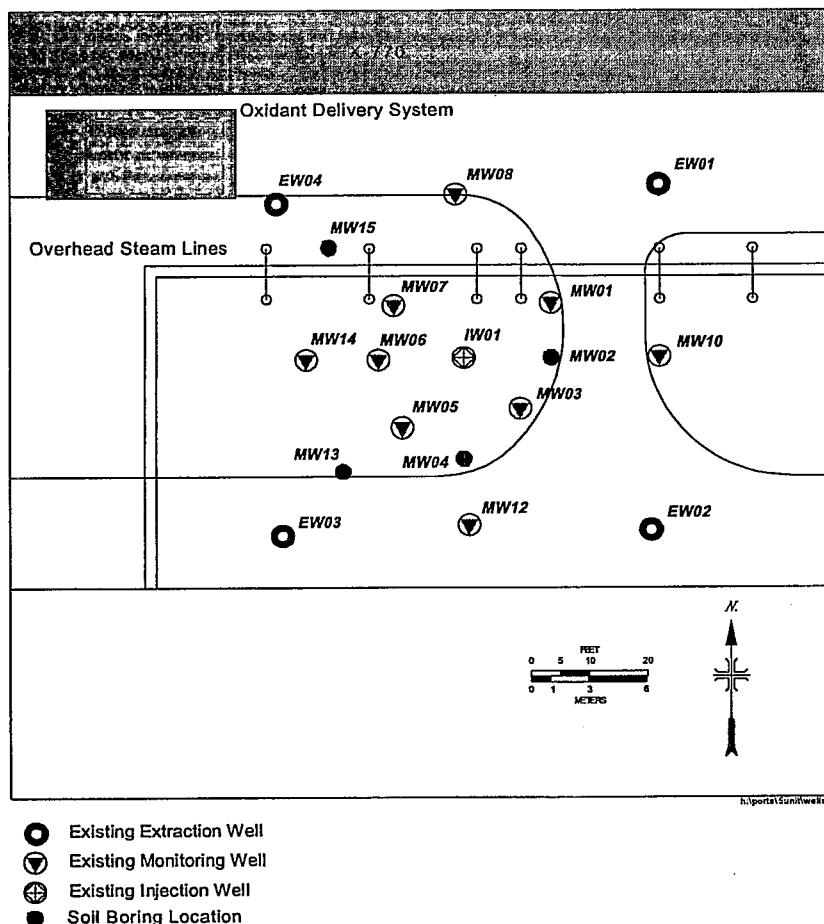- ⊕ Existing Injection Well
- ● Soil Boring Location

Figure 2. Field pilot test site.

during recirculation, and contaminant concentrations were monitored daily. Additional analyses for cations, anions, and water quality parameters were collected during recirculation of the first pore volume, but terminated after delivery of the oxidant throughout the test area due to interferences in the analysis method.

During injection and recirculation, oxidant solution was injected into the Gallia through the central well and extracted at equal rates from the 4 perimeter wells located at 45 ft from the central injection well. Groundwater was extracted from the four perimeter wells at a maximum combined rate of 18 gpm (4.5 gpm from each extraction well). Groundwater from the four extraction wells was pumped through a manifold system into a single line where the $NaMnO_4$ solution was added with an oxidant-resistant chemical metering pump. The metering pump was adjusted to feed the concentrated stock solution at a rate sufficient to maintain 250 mg/L of $NaMnO_4$ in the injection water. The oxidant-laden water was then pumped into a 120 gal holding tank providing approximately 7 minutes of resi-

dence time for the oxidant with the contaminated groundwater. This ensured that only treated water was re-injected into the aquifer. Injection of the extracted water was permissible as long as the extracted water had been "treated".

A 250 mg/L $NaMnO_4$ solution was recirculated at 18 gpm for the 1st pore volume (approximately 82,000 gals or 3 days). Then the recirculated water with residual $NaMnO_4$ was supplemented with approximately 100 mg/L of $NaMnO_4$ solution to maintain a delivery of ~200 to 250 mg/L of oxidant into the region at 18 gpm for the 2nd and 3rd pore volumes. Approximately 78 gals of 40wt% $NaMnO_4$ (162.4 kg $NaMnO_4$) were delivered throughout the test region within 10 days. Approximately 240,660 gals of treated groundwater were recirculated. The recirculation flow rates remained steady throughout the test duration with ~1 gpm reduction in total recirculation flow rate over the course of the 10-day test (Table 1). This gradual but minor decline in the total recirculated flow rate is attributed to injection or extraction well fouling, matrix plugging, pump performance, or clogging/plugging within the sys-

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Table 1. Summary of Process Operation Parameters.

Location	Ave. Flow Rate (gpm)	Ave. Pressure (psi)
X770-IW01	17.37	14.5
X770-EW01	4.17	65.4
X770-EW02	4.39	146
X770-EW03	4.36	146
X770-EW04	4.59	150

Table 2. Single Well Aquifer Testing Results.

Well Number	Ave Pre-Inj ft/day	Ave Post-Inj ft/day
X770-EW02	26.5	26.7
X770-EW03	86.5	87.3
X770-EW04	44	54.3
X770-MW01	148	94
X770-MW03	297.5	271.7
X770-MW05	691.5*	532.3
X770-MW07	202.5	187.7
X770-MW08	121	143
X770-MW10	145	113.7
X770-MW12	—	366.3
X770-MW14	601.5*	337

tem lines (at in-line valves, gauges, etc). Pressures within the system and at the injection well gradually increased over time. The injection pressure at the well head nearly doubled, from 10 psi to 18.5 psi, but remained within safe operating ranges based on optimum flow out of the selected well screen, potential fracturing of the formation, and potential damage to the well construction. It is likely that the gradual increase in system pressures and decline in extraction well flow rates is in part, a result of injection well performance or potential redistribution of fine particles in the formation near the well.

Performance assessment was based on TCE reduction as determined by characterizing contaminants in the aqueous phase before and after treatment. If VOC mass was substantially reduced by oxidation, then the TCE aqueous levels in the extraction and monitoring wells should also be substantially lower. Groundwater was recirculated through the pilot test area until sufficient oxidant had been delivered or breakthrough of the residual oxidant at the injected concentration (indicating that the $NaMnO_4$ was not being consumed in the aquifer) was observed. The TCE concentrations in the test area were monitored during recirculation and for 24 hrs after recirculation was terminated. Finally, post-treatment groundwater concentrations were monitored weekly for approximately 1 month and once at 2 months after recirculation to determine the potential aquifer rebound effects.

Results

A pressure injection test conducted at the injection well (Bouwer and Rice 1976 and Horner, 1951) indicated that the injection well could sustain recirculation rates up to 26 gpm without exceeding optimum pressures at the well head. Observation of water level fluctuations during the pressure injection test also indicated significant variability in hydraulic conductivity across the 64-ft by 64-ft test area. In relative terms, greater water level increases indicate regions of higher permeability while smaller water level increases indicate regions of lower permeability. Single well tests confirmed the variability and provided a relative measure of permeability with values ranging from approximately 26 to >300 ft /d (Table 2).

Bromide tracer test results confirmed the hydraulic tests and indicated that the Gallia is very heterogeneous throughout the test region. The bromide curves from the northern wells tend to flatten out indicating a more hetero-

geneous flow system and greater dispersion while the curves to the west and south indicate a more pronounced (i.e., sharp) bromide front suggesting a more homogeneous flow system with less dispersion (Figure 3). Additionally, bromide rapidly moved (within two hours) in a southeastern direction as delineated by well X770-MW03, but was not initially detected in X770-EW02, the southeastern most well, until 10 hours after injection with the curve peak at ~22 hours after injection. Water levels, measured continuously by a data acquisition system, indicate that the system reached hydraulic equilibrium within a few hours after recirculation was initiated and remained constant throughout the test.

The bromide tracer test also provided insight on the preferential flow paths within the region. Based on preliminary calculations (assuming laminar plug flow and homogenous subsurface conditions) and model predictions (WinTrans) it was estimated that it would take approximately 3 days for the tracer to reach each of the extraction wells located 45 ft away. However, initial detection of the bromide in the extraction wells was within 5 to 10 hours. The tracer was detected at the northeastern well (X770-EW01), but bromide concentrations did not exceed 5 mg/L (near the minimum detection limit of the field probe). Thus, the majority of the water produced from X770-EW01 is presumed to be from outside the test region as indicated by the slow delivery of bromide and oxidant to the well. In relative terms, the region north and east of X770-EW01 appears to be more permeable than the region between the injection well and X770-EW01, including X770-MW10. Finally, the rapid arrival of the bromide tracer at the western extraction wells and the slow arrival at northeastern well illustrates how preferential flow zones control movement of fluids through the Gallia.

Groundwater samples collected prior to system operation indicated TCE concentrations ranged from 133 mg/L to 2148 mg/L with higher concentrations detected in the northern and western monitoring wells. Soil samples ranged from 3 to 4527 mg/kg, typically with increasing concentrations with depth. Oxidant injection using vertical wells in a 5-spot pattern was capable of providing sufficient hydraulic control to deliver oxidant throughout the

permeable zones of the Gallia within the pilot test area within 3 days or less. The pre-test TCE concentrations throughout the region were reduced to <10 mg/L throughout all but the lower permeable eastern edge of the test region within 3 days indicating an apparent reduction in contaminant levels of ~92% (Figure 4). Continued recirculation for 10 days, provided uniform oxidant delivery throughout the entire area excluding the northeast extraction well (X770-EW01). As of two hours after recirculation was terminated, TCE concentrations were reduced to below detection limits (5 mg/L) at all but one location, (from ~1500 mg/L to 650 mg/L at X770-EW01), indicating an apparent ~97% reduction in TCE. When the TCE concentrations are compared to delivered oxidant concentrations (Figure 5) at the same time intervals, the correlation of

oxidant delivery with TCE reduction is apparent. The slower arrival of oxidant to the northeast portion of the region (specifically X770-EW01 and X770-MW10) is also noticeable and attributed to the lower permeability of this region. It is important to note that while the permeability of the Gallia varied by over an order of magnitude in the region (Table 2), that oxidant was effectively delivered throughout the area in a relatively short time frame (i.e., 3 days).

To evaluate the short term effects of the residual oxidant and TCE within the region, groundwater samples were collected at 1, 2, 4, 6, 9, 21, and 27 hrs after system shut down. Additionally, groundwater samples were collected weekly for one month after recirculation. Although low levels of TCE were present along the upgradient edge of the
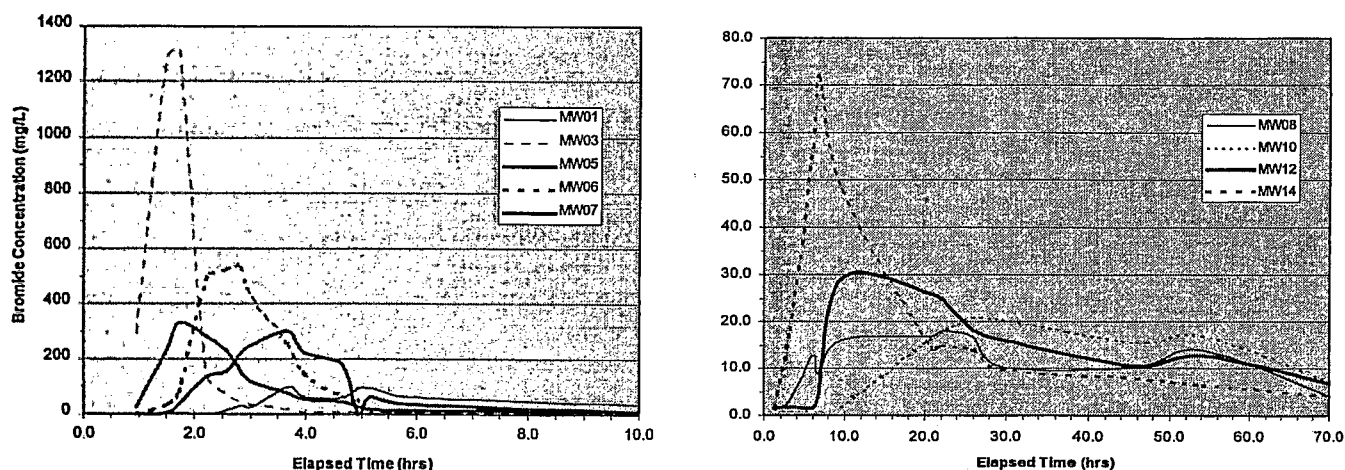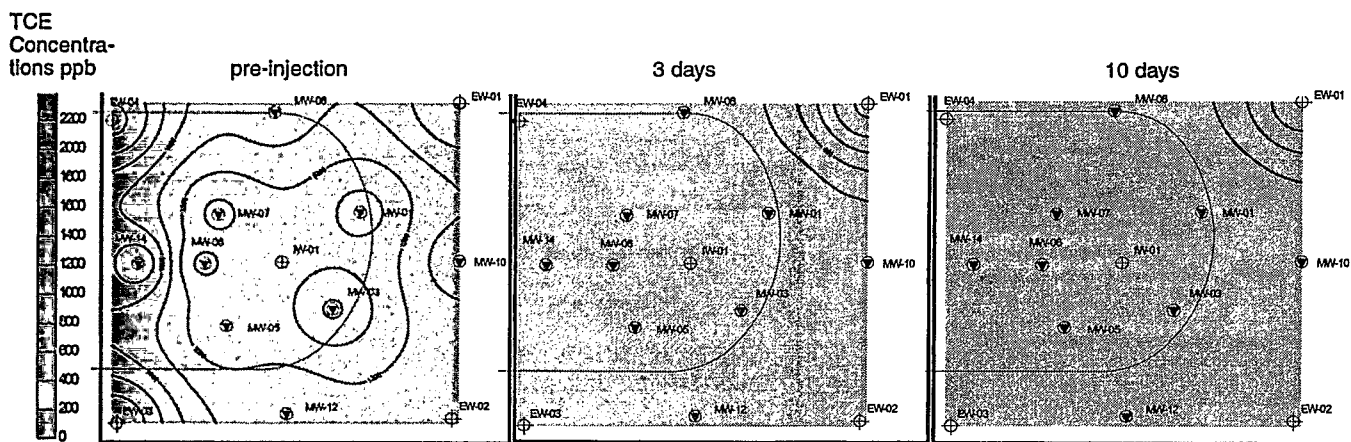

Figure 3. Bromide curves.

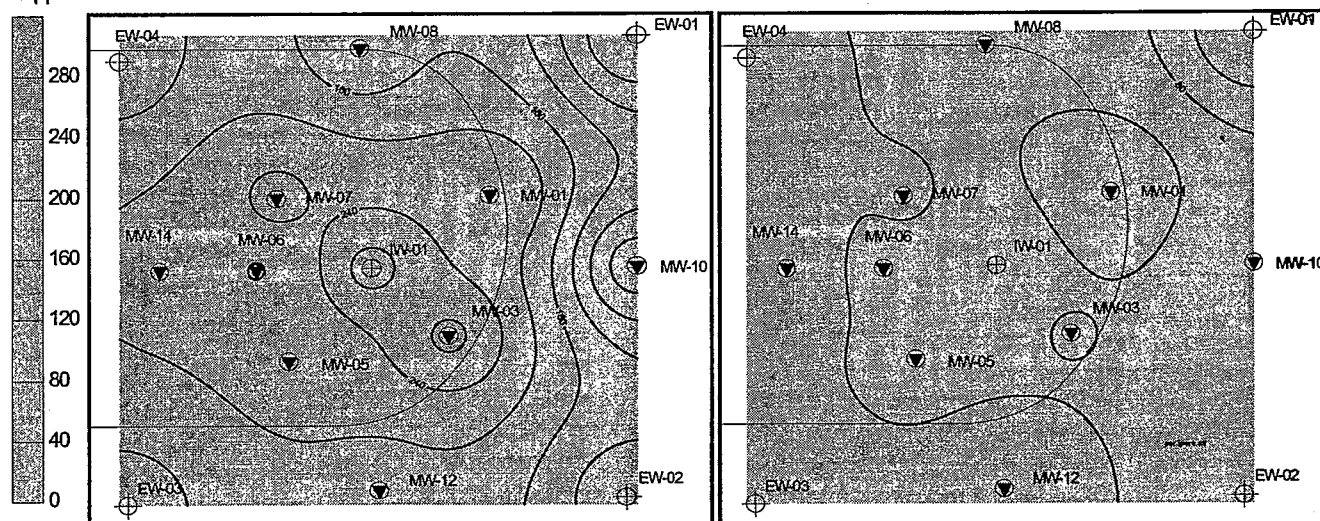Figure 4. TCE distribution within the pilot test area.

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Figure 5. NaMnO$_4$ distribution within the pilot test area.

test area (14 mg/L at X770-MW08, 39 mg/L at X770-EW04 and up to 738 mg/L at X770-EW01) when the system was shut down, the TCE concentrations continued to decline after recirculation was terminated. This decline in TCE concentrations is due to the oxidation of organic compounds by the oxidant remaining in the pore spaces. TCE remained near or below detection limits (<20 mg/L) for approximately two weeks after recirculation at which point the TCE concentrations along the upgradient northern edge (X770-EW01, X770-MW08, and X770-EW04) and lower permeable eastern edge (X770-MW10) of the test area began to increase (Table 3). The higher concentrations detected at these locations can be attributed to the migration of untreated upgradient plume groundwater into the test region (northern edge) as well as TCE diffusion

from the less permeable zones of the test area (eastern edge). It is important to note that near the injection well (15 ft radius monitoring wells) where the delivered oxidant mass was the highest, TCE concentrations remained below detection limits one month after recirculation except at the most upgradient location (35 mg/L at X770-MW01).

One month after system shut down, the oxidant concentrations within the region had declined to less than 1 mg/L while a gradual increase in TCE concentrations was observed. However, the apparent TCE mass reduction within the mobile groundwater fraction of the test cell remained at ~83%. The oxidant consumption over time is as expected and presumed to be due to a combination of factors including oxidation of the natural organic material present

Table 3. TCE Concentrations (in mg/L) throughout the Pilot Test Area at Selected Intervals (see Figure 2 for well locations).

	Pre-test baseline (average)	3 days after injection (one pore volume)	End of inj/rec. (10 d or 3 pore volumes)	2 hours after shutdown	2 weeks after shutdown	4 weeks after shutdown
X770-MW01	820	ND	ND	ND	8	35
X770-MW03	462	ND	3	ND	ND	ND
X770-MW05	904	2	4	4	ND	ND
X770-MW06	724	ND	ND	ND	ND	ND
X770-MW07	895	7	ND	1	ND	ND
X770-MW08	1433	8	14	ND	70	205
X770-MW10	1420	72	2	48	553	610
X770-MW12	1270	3	ND	5	ND	ND
X770-MW14	1591	8	9	28	ND	10
X770-EW01	1605	1043	738	340	1421	1461
X770-EW02	1164	20	9	ND	7	6
X770-EW03	2148	37	8	11	ND	ND
X770-EW04	2040	40	39	3	132	355
X770-IW01	133	41	78	ND	7	18

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and any TCE that was diffusing from the finer grained less permeable zones in the Gallia or the overlying Minford and advecting from the upgradient contamination into the test area.

Efforts to examine reaction intermediates and products (e.g., chlorinated organic acids or partially degraded chlorocarbons) as well as system toxicity have been initiated and revealed no adverse effects. For example, using a Microtox Model 500 analyzer (AZUR Environmental, Carlsbad, CA), groundwater samples were analyzed for acute toxicity to a luminescent bacteria (*Vibrio fischeri*) when exposed to 91% of the total sample concentration. No toxicity was measured for background or post-recirculation samples.

Single well tests were repeated at each monitoring location at the end of the pilot test to quantify any potential formation plugging, possibly due to MnO_2 generation and the potential redistribution of fines within the matrix. Post injection/recirculation hydraulic conductivity values ranged from 26 to 530 ft/d and were not significantly different from the pre-test values (Table 2).

Conclusions

Oxidant injection using vertical wells in a 5-spot pattern was capable of providing sufficient hydraulic control to deliver oxidant throughout the permeable zones of the Gallia within the pilot test area within 3 days. Pre-test baseline TCE concentrations were reduced to <10 mg/L throughout all but the lower permeable eastern edge of the test region within 3 days indicating an apparent reduction in contaminant levels of ~92% within 3 days and ~97% reduction at 10 days (2 hours after the end of the test). This oxidant delivery technique is applicable to relatively permeable, saturated subsurface media contaminated with dissolved and sorbed phase contaminants and potentially ganglia of non-aqueous phase liquids (NAPLs). An underlying aquitard is required in order to prevent spread of contamination during the injection phase. It is noted that application to situations with large masses of NAPLs (e.g., pools) may require substantially higher oxidant loadings and potentially modified hydraulic control approaches.

The costs of the 5-spot ISCOR will vary depending on the scale of the application and the performance goals required. A major cost savings with the recirculation delivery method is avoidance of costs associated with treatment and discharge of extracted groundwater, which in this pilot test was ~240,000 gal. The estimated cost per gallon of treated groundwater during the pilot test at a DOE facility was ~$1.70/gal, including well installation costs but excluding PORTS site support (e.g., health and safety, health physics, construction engineering, waste management, and project management oversight). While it is important to recognize that specific site conditions will greatly influence the cost, the most significant costs associated with the 5-spot ISCOR approach are well installation and the oxidant. The cost of the injection wells and extraction

wells will be dependent on the size, depth, location, and materials as well as the drilling subcontractor. The cost of the oxidant will be dependent on the oxidant concentration delivered to the subsurface over some period of time based on performance goals and initial contaminant concentrations.

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In-Well Aeration/Stripping Technology: Oveview and Performance Results

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In-well stripping is an *in situ* remediation technology for VOCs in groundwater that can be applied as an alternative to pump/treat systems. This presentation provides a summary of in-well stripping technology along with performance data from several sites.

Summary of Technology

In-well stripping technology relies on pressurized air to circulate and clean water flowing through a well. A pressurized air delivery line is placed in the well to deliver a stream of air bubbles into the well. The rising column of bubbles acts as an air-lift pump pushing the combined stream of air/water up the casing while drawing contaminated water in through the extraction screen. As the air bubbles and water move up through the casing, volatile contaminants transfer from an aqueous dissolved phase to a vapor phase in the air bubbles. A vacuum line is applied at the well head at a point above the packer to recover contaminant vapors for treatment. A typical layout of a stripping well is shown in Figure 1.

The casing is perforated above and below the packer with an upper screen (the recharge screen) to allow the groundwater to flow back into the aquifer. Modeling studies have predicted and experimental studies have verified that the reinfiltrating water completes a toroidal circulation pattern within the aquifer. This permits a large portion of the water to be drawn back in and reprocessed. The water discharging from the treatment well contains elevated levels of dissolved oxygen (typically at or near saturation). Some of the important criteria for proper system design and implementation include the hydrogeologic circulation patterns, mass transfer efficiency of the in-well stripping, and geochemical stability calculations.

Case Studies

Performance data are available from operating in-well stripping systems at a variety of sites. An example data set is presented for a single project (site background, geologic and hydrogeologic conditions, and concentration reduction profiles). Additional summary performance data for other sites is also presented.

The case study presented is for an industrial site in Seattle, Washington. The property was utilized for manufacturing operations and groundwater beneath the site is contaminated with TCE. Operations were discontinued in the late 1970's and contaminated soil was discovered in the mid 1980's.
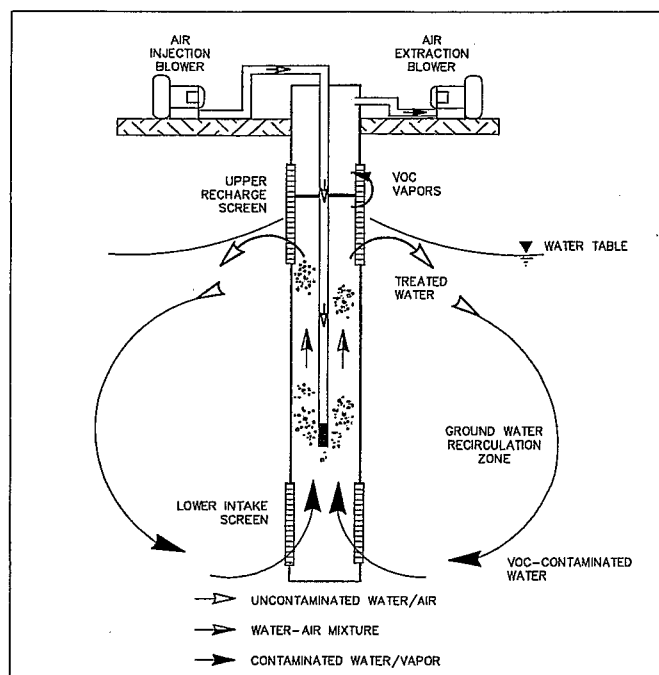

Figure 1. Example In-well Stripping System

The VOCs present in groundwater at the site include TCE and several degradation byproducts. The observed distribution and relative concentration ratios indicates that significant degradation of TCE is occurring. Based on site conditions and plume distribution, the half life for TCE is estimated to be 0.4 years (assuming a first-order decay process). The maximum TCE concentration detected in water was at the solubility limit. Other important geochemical considerations at this site include the presence of dissolved iron and the equilibrium of calcite ($CaCO_3$) with respect to the groundwater.

The treatment system is comprised of two Density Driven Convection (DDC) treatment wells and several performance monitoring wells. Monitoring activity includes characterization of VOCs in the inlet and outlet at each treatment well as well as sampling from 12 monitoring wells. All monitoring has been conducted on a quarterly basis for the duration of system operation.

The site geology consists predominantly of unconsolidated sand and silt to a depth of about 35 ft. The sediments are relatively homogenous in an areal extent. However, discontinuous silt layers are encountered indicating significant heterogeneity over the vertical profile. The bottom portion of the aquifer (~35 to 45 ft bgs) grades from an interbedded silt layer to a competent clay unit.

The hydraulic conductivity of the aquifer has been estimated at 10^{-2} cm/sec (28 ft/day) based on an aquifer pumping test. One of the treatment wells is completed into the interbedded silt unit and the well yield is an order of magnitude less than the well completed in the aquifer material (2 gpm versus 20 gpm). The hydraulic gradient ranges from about 0.004 to 0.007 ft/ft.

Since the site was suspected to contain a TCE NAPL, the treatment well was configured to collect DNAPL in a reservoir at the bottom from which it can be pumped to the surface and removed as a separate phase liquid. Upon startup of the system, separate free-phase NAPL was recovered at a rate of approximately 1 liter/day. Recovery of NAPL continued for about six weeks of operation and declined to zero over the operating time. Total NAPL recovery was approximately 26 liters. The physical mechanism inducing the DNAPL migration to the well is thought to be the cyclical pumping of the recirculating well and the constant vibratory energy into the aquifer formation. This energy can cause the NAPL ganglia to coalesce and migrate towards the recirculating well. When the well was not operating, no TCE NAPL accumulated in the well.

Site Cleanup Standards

The site and all surrounding areas are industrial properties. Groundwater at the site and in the local area is not a potable resource and water supply wells are not allowed in the area under State regulations. The risk assessment completed in the RI/FS identified the reasonable maxi-

mum exposure for groundwater as discharge to surface water in the nearest river (approximately 4000 feet from the plume and 2000 from the property boundary).

Based on the reasonable maximum exposure for groundwater, cleanup levels for groundwater established in the RI/FS have been based on applicable surface water quality criteria. The specific standards for protection of beneficial use of surface water are from EPAs Water Quality Criteria Guidance Documents. The cleanup goals are:

- Trichloroethene—2 mg/L based on the Lowest Observed Effects Level (LOEL) for marine organisms (Federal Register Notice 45 FR 79341).

- 1,2 Dichloroethene—224 mg/L based on the LOEL for marine organisms (Federal Register Notice 45 FR 79332).

- Vinyl Chloride —0.525 mg/L based on the ambient criteria for human-health fish consumption (Federal Register Notice 45 FR 79341).

Performance Data

The monitoring data collected over the first 18 months of system operation are presented in Figure 2. These three wells represent the central area of the TCE plume and cover the expected area of influence from the treatment wells. The concentration reductions observed in the performance monitoring wells are significant. Three of the performance monitoring wells have had TCE concentration reductions of greater than 99%. Based on the observed concentration reductions (99+% reduction at about 60 feet away), the radius of the treatment zone is estimated to be more than 2 times the distance from the inlet screen to the water table. The mass removal for the system has been monitored based on NAPL recovery and off-gas VOC concentrations. Mass removal during the first 6 months of system operation is estimated to have been 400 lbs.

TCE concentration in the one treatment well where NAPL was recovered has been reduced by about 80%. The TCE concentration in the other treatment well has been quite variable with concentrations generally increasing as the higher VOC concentrations are drawn up from the interbedded silt zone. TCE is the primary VOC present in this central area of the plume. The other VOCs present (i.e., degradation products cis-1,2 dichloroethene and vinyl chloride) have generally shown significant concentration reductions but the results are more variable.

A portion of the VOC plume (consisting primarily of the degradation products cis 1,2 DCE and vinyl chloride) extends beyond the recirculation zone established by the treatment wells. The longer-term plan for site remediation and closure is to operate the treatment system for source control and mass removal to the extent that continued operation is practical and effective (continued concentration reductions are observed). After a point of diminishing
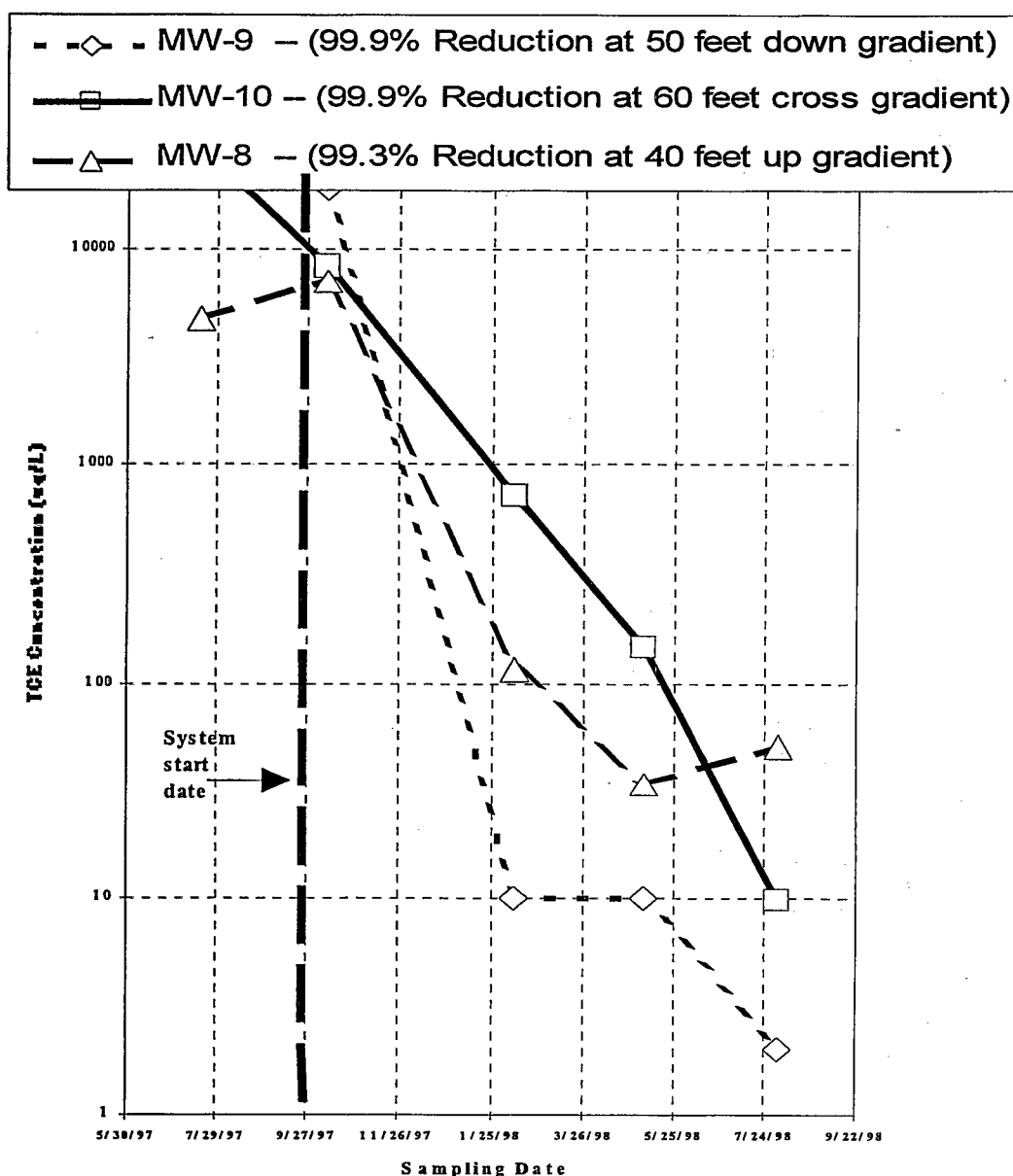
Figure 2. Monitoring data-TCE concentration deductions.

returns is reached, the active remediation will be stopped and transitioned into monitored natural attenuation.

Performance data are also available from other sites from other industries. One example is a light industrial facility located in the city of Coeur d'Alene. Groundwater beneath the site is contaminated with TCE as a result of past waste disposal practices at several different industries in and around Coeur d'Alene. The layout of site monitoring wells includes one well at the outlet of the treatment well (screened over the water table), one well 19 feet away (screened from 5 to 15 feet below the water table) and

another 89 feet away (screened from 10 to 20 feet below the water table). The inlet screen is placed at a depth of 30 feet below the water table and the recharge screen is placed at the water table. The system operates at a water pumping rate of 35 gpm. Groundwater at the site is encountered at about 190 feet below ground surface.

The maximum groundwater concentration of TCE identified at the site was 1510 mg/L in a sample taken during drilling. A sample taken just before the system began operating (October 22 1996) had a concentration of 900 mg/L.

The monitoring data collected over the first 12 months of system operation are presented in Figure 3. The concentration reductions observed in nearby monitoring wells are quite dramatic. The closest monitoring well (MW-1, 19 feet away) has shown TCE concentrations reduced by 98 percent in the initial operating period. The most distant monitoring well (MW-3, 89 feet away), has shown concentration reductions of 96 percent in over 12 months and the downward trend in concentration appears to be continuing. Based on the observed concentrations reductions (96% reduction at about 89 feet away), the radius of treatment zone is more than 3 times the distance from the inlet screen to water table.
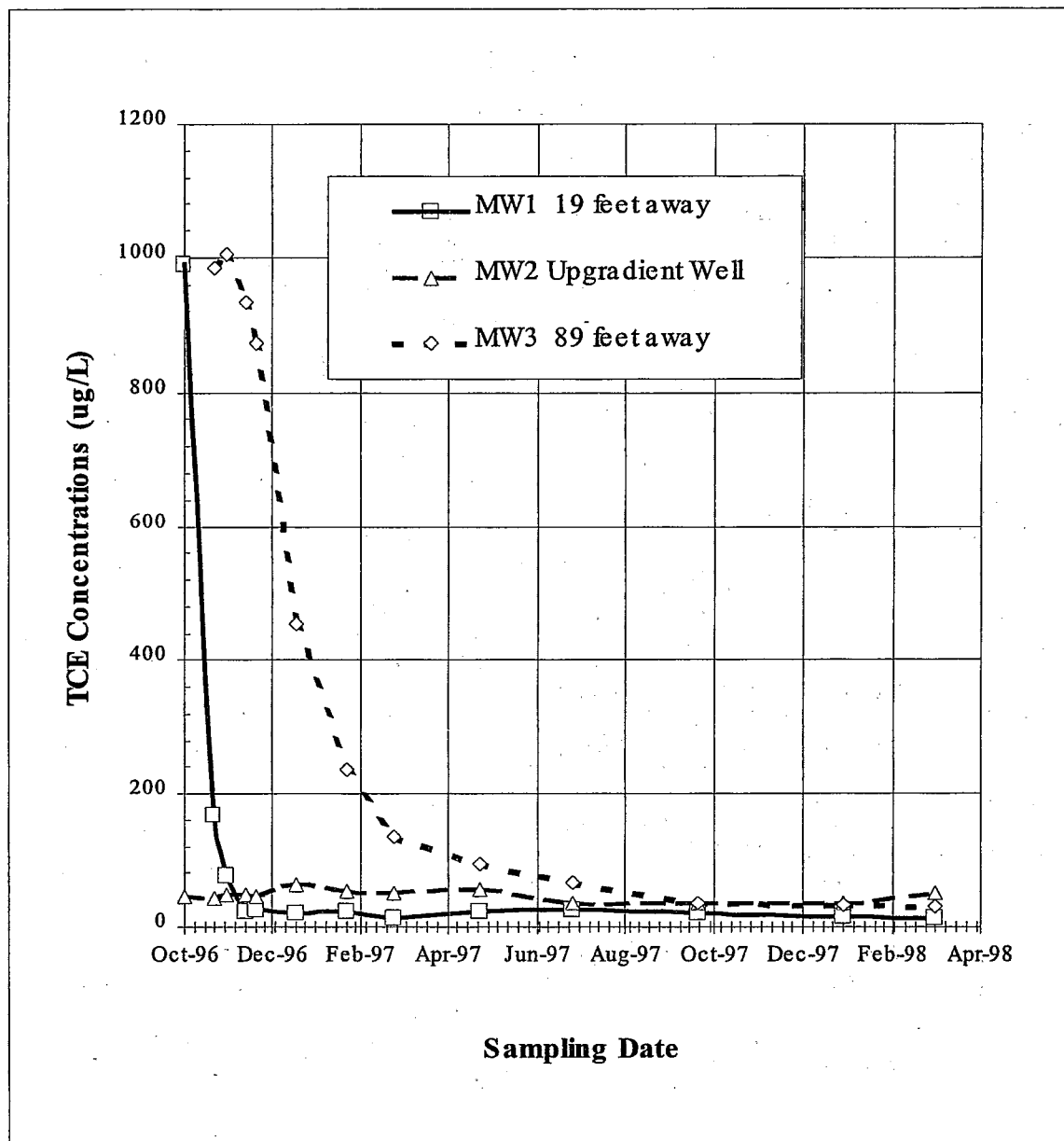

Figure 3. Monitoring data.

Air Sparging for Groundwater Remediation of Toluene and Other VOCs: Case Studies

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Air Sparging (also called *In situ* Air Sparging, IAS) is an *in situ* technique being used more and more commonly for the *in situ* treatment of groundwater in the saturated zone contaminated with volatile organic compounds. This presentation will:

- describe AS and how it works,
- explore the types of site conditions that AS is applicable to,
- discuss the information needed to design a appropriate AS system,
- the advantages of AS over other remedial methods,
- the operating results from three AS systems.

Implementation of AS consists of injecting air below the water table to strip (transfer) volatile organic compounds (VOC) from the dissolved and adsorbed phases to the vapor phase. The injected air now containing the VOC rises up to the vadose zone and eventually the atmosphere. In many cases, soil vapor extraction (SVE) is used in conjunction with AS in order to collect and treat these VOC-containing soil vapors before they are emitted to the atmosphere. Gas transfer of oxygen also occurs from the injected air to the groundwater. In this way, AS can oxygenate groundwater, increasing the redox potential and the dissolved oxygen content. This dissolved oxygen can stimulate aerobic biodegradation of biodegradable contamination in the saturated and vadose zone. These processes of biosparging and bioventing will not be addressed, since this conference deals with the abiotic processes of AS.

The types of conditions where AS is most applicable include:

- Sandy or permeable silty sand soils;
- Homogeneous, non-stratified soils;
- VOC only contaminated sites.

The most critical aspect affecting successful AS is the presence of heterogeneous soil that permits short-circuiting and preferential flow, thereby not remediating all areas and depths. Additional information on AS can be obtained from many sources, including the *In situ* Air Sparging Engineer Manual of the US Army Corps of Engineers (EM-1110-1-4005).

The three AS sites to be discussed have the following characteristics:

- each about 1 acre in size;
- contaminated with toluene and/or volatile ketones;
- relatively homogeneous fine sand soils

AS has already remediated one of sites while the other two sites have been undergoing air sparging for one and two years respectively.

- Site data to be presented evaluated will include:
- System design features
- Groundwater concentrations and plume size changes over time;
- Increase in dissolved oxygen from dissolution of sparge air;
- Prevention of groundwater migration through use of a "curtain" of AS points;
- Differences in removal rates for compounds with different Henry's Law constants;
- Typical problems with AS and innovative solutions.

Application of VFLUX to Assessment of Soil Venting Performance and Closure

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Remediation Zone Paradigm

Evaluation of mass flux to and from groundwater is vital in integrating venting application with progress in ground-water remediation. Soil remediation goals must reflect the realities of ground-water remediation. As illustrated in Figure 1, subsurface remediation are partitioned into three distinct zones for performance evaluation purposes. Zone 1 is bounded on the upper end by the soil surface and on the lower end by the seasonally high capillary fringe. It consists of consistently unsaturated media (above region of water table fluctuation) where mass flux to and from the capillary fringe occurs through infiltration and diffusion, and mass flux from the capillary fringe to the vadose zone occurs through diffusion. Exclusion of water table fluctuation allows considerable simplification of unsaturated flow and transport in this zone.

Zone 2 consists of media periodically de-saturated due to water-table fluctuation or dewatering. Often, it will consist of a highly contaminated "smear" zone containing residual NAPL where venting is combined with dewatering to remove contaminant mass from a localized region. Zone 2 is bounded on the upper end by the seasonally high capillary fringe and on the lower end by the maximum depth of the capillary fringe during ground-water dewatering. The base of zone 2 is located between ground-water extraction wells to ensure minimum dewatering to the depth of interest. The maximum depth of zone 2 will be dictated by the vertical profile of contamination and feasibility of dewatering to the depth of interest. If a smear zone exists in highly permeable media where dewatering is infeasible or requires large pumping rates, zone 2 can be thought of as the region where another source control technology such as sparging is used. If dewatering is not to be used in conjunction with venting, then zone 1 is directly linked to zone 3.

Zone 3 is bounded on the upper end by the capillary fringe during dewatering and on the lower end by the maximum depth of ground-water remediation. It represents media that remains saturated during venting. Ground-water concentrations in zone 3 vary temporally and determine compliance in zones 1 and 2. Zone 2 is in compliance when ground-water concentrations are less than or equal to ground-water concentrations in zone 3. This ensures that remediation of groundwater within a smear zone will be attempted to levels consistent with deeper contamination. This avoids reduction of ground-water concentrations in zone 2 to levels lower than what would occur through vertical recontamination from zone 3.

In the case of a light non-aqueous phase spill where ground-water concentrations within a "smear" zone are at much higher levels than beneath the smear zone, low concentrations in zone 3 forces aggressive dewatering and venting application in zone 2. In the case of a dense non-aqueous phase spill where ground-water concentrations may be at high levels deep within an aquifer, remediation within the dewatered region or zone 2 proceeds only to the degree at which it is consistent with remediation in deeper regions or zone 3. Zone 1 is in compliance when mass flux to zone 2 through vapor diffusion and infiltration is less than the mass flux from zone 2 to zone1 through vapor diffusion. This ensures aggressive venting application in the vadose zone when groundwater has very low levels of contamination, and less aggressive venting application when vapor diffusion will result in recontamination of cleansed soils. Venting performance for zones 1 and 2 thus is dynamically linked to the performance of ground-water remedial efforts in zone 3. Substantial progress in remediating groundwater translates to increasingly stringent soil venting performance standards, while lack of progress in remediating groundwater translates into
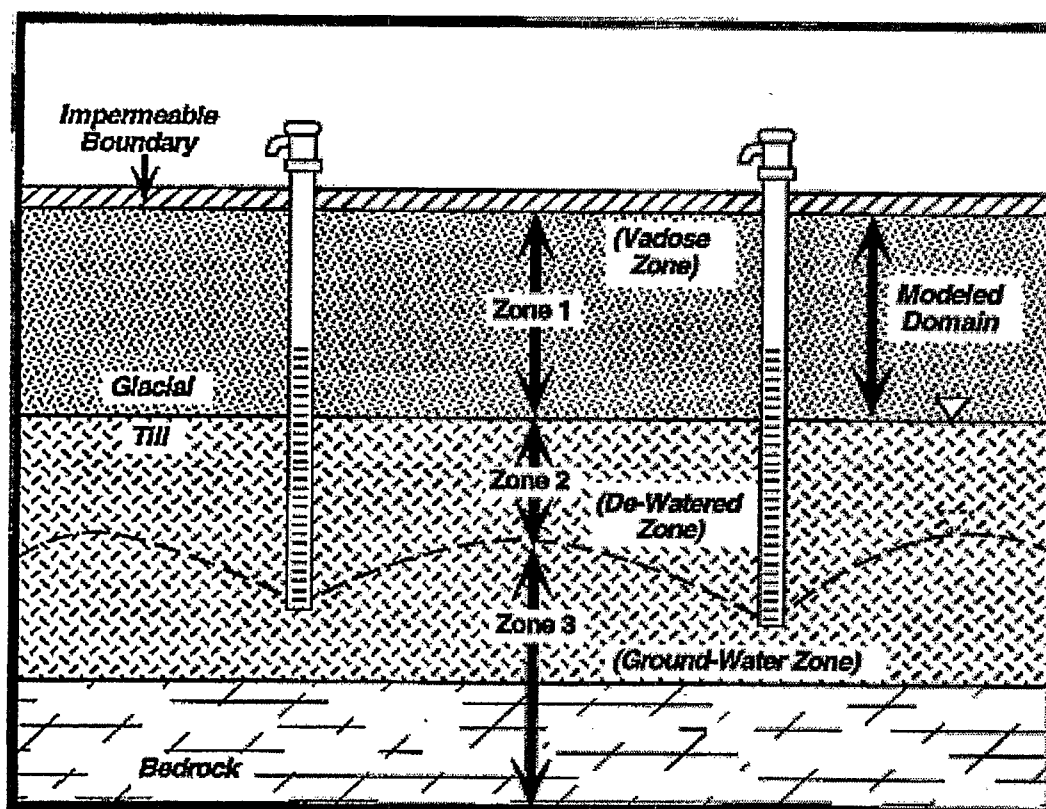
Figure 1. Schematic of three remediation zones.

less stringent soil remediation requirements. Regardless of the strategy chosen to close an SVE site, there must be a link between ground-water and soils remediation. Unfortunately, this aspect of closure is missing at most sites.

Modeling Approach

Mathematical models that simulate soil-water movement to groundwater vary in complexity from simple and conservative algebraic water-balance equations that neglect degradation and volatilization to more process descriptive finite-difference and finite-element numerical codes incorporating Richards' equation. Vadose zone modeling should ideally: (1) be rigorous enough to incorporate major fate and transport processes, (2) have input parameters that can be readily collected prior to and during venting operation, and (3) be sufficiently user-friendly to enable use by consultants and regulators. Unfortunately, simultaneous attainment of all of these goals is unrealistic. Lack of data to support spatial discretization of soil properties (e.g., capillary pressure parameters, hydraulic conductivity, porosity, bulk density, moisture content, total organic carbon content) and contaminant distribution, however, commonly limits the use of sophisticated mathematical models. One approach to this problem is to use fictitious but "reasonable" input for numerical two- or three-dimensional modeling. Another approach, which is perhaps more practical and pursued here, is to start with the data at hand and use fairly simplistic one-dimensional analytical modeling with the assumption of constant infiltration to gain insight into the potential magnitude of solute transport to groundwater. More sophisticated numerical modeling can then be utilized if additional supporting data becomes available. Regardless of sophistication, all modeling is a simplification of reality containing considerable uncertainty in simulated results. Uncertainty analysis is critical in assessment of model output. It is for this reason that a venting closure strategy or any other vadose zone problem decision matrix should include provisions for consideration of other factors. For the assessment of venting performance and closure, these factors include assessment of site characterization, design, monitoring, and rate-limited vapor transport.

To meet the needs of mass flux assessment, an analytical model termed VFLUX denoting vertical flux simulation, has been developed. VFLUX is similar to the well known model, VLEACH commonly used in the Superfund program for vadose zone solute transport assessment except that it allows for the presence of non-aqueous phase liquid residual in soils, degradation, and a time-dependent boundary condition at the water table interface. The time-

dependent boundary condition is the centerpiece of the mass flux assessment because it dynamically links performance of ground-water remediation to vennnting closure. VFLUX a significant improvement over VLEACH because of these increased capabilities and exact method of solution. The governing equation with associated initial and boundary conditions of VLEACH was solved numerically, even though it could have easily been solved analytically. The determination of mass flux requires calculation of a spatial derivative at the water table interface, which is prone to large error when spatial discretization is coarse and a sharp concentration gradient exists between grid blocks. The analytical solution of VFLUX provides exact values of mass flux at any location. Also, in order to calculate concentration profiles at a specified time, the transport equation has to be solved numerically at each time step starting from the initial distribution. Analytical methods allow direct solution at the time of interest. In addition, analytical solutions are not subject to convergence and stability problems arising from the use of coarse spatial grids and large time steps. Thus, there is less chance that an inexperienced user will generate inaccurate output due to poor specification of numerical simulation criteria (e.g., grid size).

In-Situ Treatment of Hexavalent Chromium and VOCs Using Recirculating Wells

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Project Performance Corporation (PPC) has implemented a pilot test of the Enhanced Density-Driven Convection (EDDC) technology at the Boomsnub/BOC Gases Superfund Site in Vancouver, Washington. The pilot test work was funded by EPA Region 10. At this site, the EDDC technology is being used for treatment of a plume containing halogenated volatile organic compounds (VOCs), as well as hexavalent chromium [Cr(VI)]. In-well air stripping is being used to treat the VOCs and a chemical reductant, sodium hydrosulfite, is being used to treat Cr(VI) by reducing it to trivalent chromium [Cr(III)]. The following abstract provides a short project summary and preliminary evaluation and interpretation of results. The following sections provide general background on characteristics of the site and EDDC system and a discussion of results of groundwater sampling and analysis.

Bench Scale Testing

Some of the initial work on the project was bench scale testing of several different chromium removal processes that could be implemented with a recirculating well. The tests included batch and column tests of different reactive media to remove the chromium in an infiltration gallery constructed at the well. The different approaches tested included the use of zero valent iron and various zeolites treated with iron. The results of the column tests indicated that the chromate could be effectively removed from solution. However, the chromate removal effectiveness for the reactive media (both zero valent iron and iron-treated zeolites) decreased significantly as the number of pore volume passed through the column increased. The reactive capacities of these media were less than 10^{-3} g chromate/ gm of reactive media. These relatively low chromate loading capacities were consistent with column experiments conducted by Envirometal Technologies, Inc. in testing conducted to evaluate the effectiveness of a permeable reactive wall at the site. Based on the relatively low loading capacity, the change-out interval for a reactive media would be to frequent (on the order of weeks to months) for

system operation to be cost-effective compared with other treatment options.

Based on the results of the bench scale testing, it was decided that continuous injection of a reducing agent was required to effectively reduce the hexavalent chromium for a pilot scale or full scale system. Various sulfur based reducing agents were considered and sodium hydrosulfite was selected for use in the pilot test.

Site Characteristics

Site stratigraphy consists of a sandy, alluvial aquifer underlain by a silt/clay aquitard. The hydraulic conductivity of the alluvial aquifer is approximately 1×10^{-2} cm/sec and the hydraulic gradient is approximately 0.003. The depth to groundwater is approximately 10 ft and the aquifer is approximately 85 ft thick. The plume is highly stratified, with contamination present at the base of the aquifer. Vertical plume characterization was conducted using direct push (Geoprobe) sampling at 10 feet intervals. The principal VOCs present in groundwater at the site are trichloroethylene (TCE) and trichlorofluoromethane (Freon-11). Maximum concentrations of these contaminants at the location of the pilot test are approximately 5,000 mg/L for TCE and 3,000 ug for Freon-11. The maximum Cr(VI) concentration detected at the pilot test location is 14,000 mg/ L in a discrete Geoprobe sample. Upgradient monitoring wells have typically indicated Cr(VI) concentrations in the range of 4,000 mg/L.

System Description

The EDDC well was operated with a pumping rate of approximately 12 gallons per minute (gpm). The air injected into the EDDC well is provided by a blower located in an equipment trailer adjacent to the EDDC well. The blower is capable of providing a maximum air flow of approximately 65 standard cubic feet per minute (scfm), for a maximum air-water ratio of 40:1 at the design pumping

rate of 12 gpm. The air returned from the EDDC well flows through a moisture separator to remove entrained liquid, is heated to increase its temperature to approximately 95ºF, and is then treated using granular activated carbon (GAC) to remove VOCs. The treated air then flows to the blower and is reinjected into the EDDC well. A small amount of carbon dioxide (approximately 5 standard cubic feet per hour) is added to the injection air to prevent calcite fouling. The moisture separator, air heater, GAC adsorbers, and carbon dioxide supply are all located in the equipment trailer.

Hexavalent chromium is being treated by injecting a solution of sodium hydrosulfite into the treatment zone in the EDDC well. This reductant solution is stored in a 300-gallon polyethylene tank adjacent to the equipment trailer and is pumped to the EDDC well using a metering pump located in the equipment trailer. The rate of reductant addition has been varied during the test, but has generally been in the range of 1.5 to 3.0 liters per hour.

Sodium bromide was added to the reductant solution to provide a conservative, nondegradable tracer in the water being recharged from the EDDC well. The purpose of the tracer was to verify that recirculation was occurring and to determine the travel time from the EDDC well to monitoring wells and piezometers. The concentration of bromide in the effluent from the EDDC well depends on the concentration in the reductant solution, as well as the pumping rate of the well and the rate of addition of reductant. The latter two parameters varied during the first part of the test as operating conditions were being optimized. Thus, the concentration of bromide in the effluent was not constant. The concentration of bromide in the reductant solution was initially selected to maintain a bromide concentration of at least 10 mg/L in the well effluent in order to provide a high confidence of detection.

Groundwater samples have been periodically collected from the EDDC well influent and effluent and from the monitoring wells. Baseline samples were collected at or before the time of startup. The wells were then sampled at approximately 1, 2, 3, 4, 6, 8, 12, 14, 16 and 18 weeks after start of operation.

Analysis of Results

The following provides a discussion of results of groundwater sampling that has been performed to date. The discussion is organized by major analyte, i.e., bromide, chromium, TCE, and Freon-11. To assist in interpretation of results, a three-dimensional, analytical groundwater flow model was used to predict groundwater flow paths and travel times. This model was used with the site and operating characteristics described above. The interpretation and analysis of the performance monitoring data have been developed by staff from Project Performance Corporation and have been reviewed by EPA's project team for the site.

Bromide tracer and other data clearly indicate that groundwater recirculation is occurring.

The number of groundwater monitoring points and sampling intervals are necessarily limited in terms of fully describing the development of the circulation cell. However, detection of bromide in the EDDC well influent and in monitoring wells was consistent with arrival time predictions from groundwater modeling. Changes in concentration of other tracers in the groundwater (i.e., sulfate from the reducing agent) are consistent with the arrival of the bromide tracer. The groundwater monitoring data describing the bromide arrival and ultimate distribution in the aquifer are also consistent with establishment of a circulation zone. This is evidenced, in part, by the results of samples from an upgradient deep monitoring point which are indicative of convergence of upgradient flow to the base of the circulation zone.

The use of a chemical reductant is effective in treating Cr(VI) to nondetectable levels in the EDDC well.

Operations to date have shown nondetectable levels of Cr(VI) in the EDDC well effluent, both with and without significant excess reductant. The Cr(VI) is reduced to Cr(III) which is still present in the treated water. The rate of chromium removal in the treatment well and monitoring wells was measured as reductions of 76% in the influent water, 75% reduction in a monitoring well 20 feet away and 45% in a monitoring well 45 feet away (total chrome). Hexavalent chrome removal rates were essentially the same as the total chrome. The rate of chromium removal in monitoring wells located a distance away from the treatment well was less than originally predicted. The specific processes causing the less than expected performance in Cr(VI) removal are uncertain. Possibilities include a solid phase Cr(VI) present on the aquifer matrix (partitioning to the soil), heterogeneity in the aquifer media resulting in silt lenses where Cr(VI) removal is diffusion limited or other unknown factors.

Concentrations of Cr(VI) in the aquifer may be controlled by the presence of a solid phase.

This phenomenon is evidenced by the apparent rebound in Cr(VI) concentrations at monitoring wells after arrival of treated effluent. The presence of a significant inventory of solid-phase Cr(VI) in the aquifer could have major impacts on the effectiveness of groundwater remediation systems. Even a low K_d value can significantly increase the number of pore volume flushes needed to remove contamination. Even with a low K_d value of 1, approximately 15 pore volume flushes would be needed to reduce dissolved-phase concentrations by 90%. Clearly, the presence of a solid phase will significantly increase the time needed for aquifer remediation. Site-specific partitioning

values have not been obtained to verify the presence of a solid phase at the site.

Use of a chemical reductant for Cr(VI) treatment may reduce the time needed for remediation by allowing in situ as well as in-well treatment.

Data collected during the period when significant excess reductant was being added to the EDDC well suggest that discharge of excess reductant resulted in *in situ* treatment of Cr(VI). If a solid-phase Cr(VI) is present, excess reducing agent to treat Cr(VI) *in situ* could reduce the time needed for cleanup. The use of excess reducing agent would need to be carefully weighed against the resulting increased sulfate concentrations.

Operation of the EDDC system has resulted in significant VOC removal.

The intake screen for the EDDC well was located in the zone having the highest concentrations of VOCs (the base of the aquifer). The TCE and Freon-11 concentrations in this influent water were reduced by 93% and 94%, respectively, during the first 12 weeks of operation. Comparison of upgradient and downgradient concentrations in groundwater indicates a VOC removal rate of approximately 99% as upgradient water passes through the treatment zone established by the circulation cell. The average TCE concentration reduction for all cross gradient and downgradient monitoring wells was 70% and this average percent reduction value includes two monitoring locations which were initially at low concentrations to start with (due to the highly stratified plume). The average TCE concentration reduction for the wells with higher TCE levels near the base of the plume was 86%.

The rate of reduction of TCE concentrations at the bottom of the aquifer may be affected by solid-phase TCE, which acts as a continuing source of contamination.

Piezometer PZ-40 and the EDDC well are both screened at the bottom of the aquifer where the highest levels of VOC contamination are found. The concentration of TCE in the sample from PZ-40 after 14 weeks is still quite high, while EDDC influent samples have shown a TCE concentration reduction of 93% over the first 14 weeks of operation. Groundwater modeling results and Br tracer data indicate slow groundwater flushing in the zone monitored by PZ-40 and a high rate of flushing in the EDDC intake zone. The effect of the rate of flushing on concentration reductions suggests additional contamination present in the solid phase. In the zone of slow flushing, dissolution/desorption of TCE from the solid phase would be expected to maintain high dissolved-phase TCE concentrations for longer periods of time. Conversely, silt lenses may exist within the treatment zone that extend the necessary treatment time frames. An understanding of the site lithology and chemical partitioning to soil is important design information in predicting the performance of the EDDC system as well as any other remedial approach for groundwater.

An Overview of *In Situ* Chemical Oxidation Technology Features and Applications

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Introduction

Subsurface contamination by toxic organic chemicals of concern (COCs) is a widespread problem in soil and groundwater at industrial and military sites in the U.S. and abroad (Riley et al. 1992; NRC 1994; Siegrist and Van Ee 1994; ATSDR 1997). To mitigate current or future risks, remediation approaches increasingly employ engineered *in situ* technologies as well as natural attenuation processes (NRC 1994; 1997; Kovalick 1998). *In situ* treatment of the source or heart of a soil and groundwater plume is being accomplished using mass transfer and recovery methods (e.g., soil vapor extraction, air sparging, surfactant/cosolvent flushing) and in place destruction methods (e.g., bioremediation, oxidation/reduction), sometimes aided by enabling techniques (e.g., soil fracturing, soil heating). For treatment of the distal regions of groundwater plumes, natural biogeochemical attenuation and permeable reactive barriers are two strategies that are evolving (USEPA 1997; NRC 1997; NATO 1998; Kovalick 1998). This paper provides an overview of chemical oxidation and its application for *in situ* treatment of contaminated sites. During the 1990's *in situ* chemical oxidation has emerged as a promising treatment method (Siegrist 1998, USEPA 1998). Many toxic organics are amenable to rapid and complete chemical destruction or to partial degradation as an aid to subsequent bioremediation. The chemistry of peroxide, permanganate, and ozone are highlighted along with the results of lab- and field-scale applications. An approach to design and implementation is outlined as well as key issues and considerations that must be accounted for. Further details will be included in a forthcoming guidance document that is under preparation by the authors and due to be published in 1999.

Chemical Oxidation of Target Organic Contaminants

Development Background

Research and development into *in situ* chemical oxidation has occurred over the past 10 years including laboratory studies, field pilot demonstrations, and full-scale applications. As of this writing, a wide variety of organic contaminants in soil and groundwater media have been successfully oxidized by peroxide, permanganate and ozone oxidants (Table 1). The key features of each oxidant system as applied *in situ* are highlighted in Table 2. Optional delivery methods are illustrated in Figure 1 while example full-scale applications of each oxidant are summarized in Tables 3 to 5.

Early studies were primarily focused on hydrogen peroxide (H_2O_2) or Fenton's Reagent (H_2O_2 plus Fe^{+2}) and most often for *ex situ* treatment of individual organics in water (Barbeni et al. 1987; Bowers et al. 1989; Watts and Smith 1991; Venkatadri and Peters 1993). Subsequently, research began to explore peroxide and Fenton's reagent oxidation as applied in soil environments (Watts et al. 1990; Watts and Smith 1991; Watts et al. 1991; Tyre et al. 1991; Ravikumar and Gurol 1994; Gates and Siegrist 1993; 1995; Watts et al. 1997).

Research was also initiated with alternative oxidants such as ozone (Bellamy et al. 1991; Nelson and Brown 1994; Marvin et al. 1998) and potassium permanganate ($KMnO_4$) (Vella et al. 1990; Vella and Veronda 1994; Gates et al. 1995; Schnarr et al. 1998; West et al. 1998; Siegrist et al. 1998a,b; 1999, Struse 1999). Field demonstrations and

Table 1. Features of peroxide, permanganate and ozone oxidants as used for *in situ* remediation[1]

| Features	Peroxide (Fenton's)	Permanganate	Ozone
Reagent Characteristics:			
Form -	Liquid	Liquid or solid	Gas
Point of generation -	Offsite, shipped onsite	Offsite, shipped onsite	Onsite during use
Quantilites available -	Small to large	Small to large	Small to large
Oxidation *In Situ*:			
Delivery Methods -	GW wells, Soil lances	GW wells, soil lances, fractur.	GW sparge wells
Dose concentrations -	5 to 50 wt. % H_2O_2	0.02 to 4.0 wt.% MnO_4	Variable
Single/multiple dosing -	Multiple is common	Single and multiple	Multiple
Amendments -	Fe^{+2} and acid	None	Often ozone in air
Subsurface transport -	Advection	Advection and diffusion	Advection
Rate reaction/transport -	High or very high	Moderate to high	Very high
Companion technol. -	None required	None required	Soil vapor extraction
Oxidation Effectiveness:			
Susceptible organics -	BTEX, PAHs, Phenols,	BTEX, PAHs, alkenes	BTEX, PAHs, phenols,
Difficult to treat organics -	alkenes	Alkanes, PCBs	Alkenes
Oxidation of NAPLs	Some alkanes, PCBs	Direct oxidation possible	Alkanes, PCBs
Reaction products -	Direct oxidation possible	Organic acids, salts, MnO_2,	Direct oxidation possible
	Organic acids, salts, O_2,	CO_2	Organic acids, salts, O_2,
	CO_2	Minimal gas evolution	CO_2
	Substantial gas evolution		Minimal gas evolution
System Effects on Oxidation:			
Effect of NOM -	Demand for oxidant	Demand for oxidant	Demand for oxidant
Effect of pH -	Most effective in acidic pH	Effective over pH 3.5 to 12	Most effective in acidic pH
Effect of temperature -	Reduced rate at lower temp.	Reduced rate at lower temp.	Reduced rate at lower temp.
Effect of ionic strength -	Limited effects	Limited effects	Limited effects
Oxidation Effects on System:			
pH -	Lowered if inadeq. buffering	Lowered if inadeq. buffering	Lowered if inadeq. buffering
Temperature -	Minor to high increase	None to minor increase	Minor to high increase
Metal mobility -	Potential for redox metals	Potential for redox/exch.	Potential for redox metals
Permeability loss -	Potential for reduction due	metals	Potential for reduction due
	to gas evolution and colloids	Potential for reduction due to	to gas evolution and colloids
		MnO_2 colloid genesis	

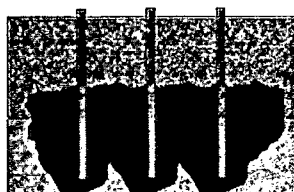The information presented is for illustrative purposes only.
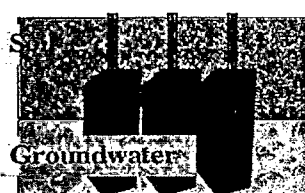
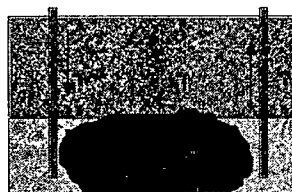Permeation with H_2O_2 or $KMnO_4$
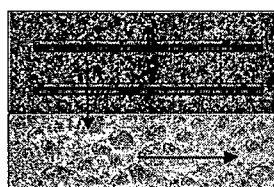
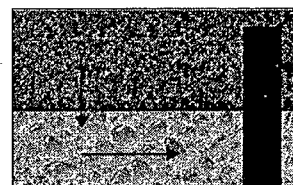Fracture sheets with Fe^0 or MnO_4^-
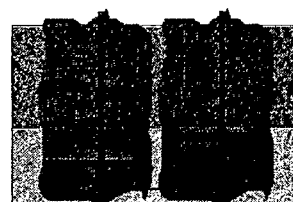
Mixing with H_2O_2 or $KMnO_4$

Sparging with ozone

Flushing with $NaMnO_4$

Treatment walls of redox solids

Figure 1. Example applications of *in situ* chemical oxidation systems that have been deployed.

Table 2. Representative list of organics successfully treated by chemical oxidants

Organic Contaminant	Media treated	Oxidant	References
Trichloroethylene	Water (spiked)	H_2O_2	Bellamy et al. 1991
	Silica sand (spiked)	H_2O_2	Gurol and Ravikumar 1992
	Silty clay soil (spiked)	H_2O_2	Gates and Diegrist 1995
	Sand & clay soils (spiked)	H_2O_2 or $KMnO_4$	Gates, Siegrist and Cline 1995
	Groundwater (spiked)	$KMnO_4$	Case 1997, Yan and Schwartz 1996
	Groundwater (field site)	$KMnO_4$	West et al. 1998, Schnarr et al. 1998
	Groundwater (field site)	$NaMnO_4$	Lowe et al. 1999
	Silty clay soil (field site)	$KMnO_4$	Siegrist et al. 1999
Tetrachloroethylene	Water (spiked)	H_2O_2	Bellamy et al. 1991
	Silica sand (spiked)	H_2O_2	Leugn et al. 1992
	Sand, clay soils (spiked)	H_2O_2 or $KMnO_4$	Gates, Siegrist and Cline 1995
	Groundwater (field site)	$KMnO_4$	Schnarr et al. 1998
	Groundwater (spiked)	$KMnO_4$	Yan and Schwartz 1996
	Groundwater (field site)	Ozone	Dreiling et al. 1998
Carbon tetrachloride and t-1,2-DCE	water (spiked)	H_2O_2	Bellamy et al. 1991
Pentachlorophenol	Silica sand (spiked)	H_2O_2	Gurol and Ravikumar 1992
	Natural soil (spiked)	H_2O_2	Watts et al. 1990
2,4-dichlorophenol, dinitro-o-cresol	Water (spiked)	H_2O_2	Bowers et al. 1989
Trifluralin, hexadecane, dieldrin	Soil (spiked)	H_2O_2	Tyre et al. 1991
Naphthalene, phenanthrene, pyrene	Clay, sandy soils (spiked)	H_2O_2 or $KMnO_4$	Gates, Siegrist and Cline 1995
Octachlorodibenzo(p)dioxin	Soil (spiked)	H_2O_2	Watts, et al. 1991
Motor oil/diesel fuel	Soil (field site)	H_2O_2	Watts 1992
PAHs and PCP	Soil and GW (field site)	Ozone	Marvin et al. 1998
BTEX and TPH	Soil and GW (field site)	Ozone	USEPA 1998

Table 3. Example applications of *in situ* treatment using peroxide (after USEPA 1998; Siegrist 1998)

Location (date) Delivery	Media and COCs	Application method and results
Ohio (1993) Deep soil mixing	Silty clay soil with TCE and VOCs.	H_2O_2 + compressed air injected during deep soil mixing to 15 ft. depth in 3 10-ft. diam. mixing zones, Up to 100 mg/kg mass reduced by 70% including 50% due to oxidation.
Colorado (1996) Injectors into GW	Groundwater with BTEX.	H_2O_2 + chelated Fe injected via 8 to 14 lances and 7 trenches over 100 ft. x 100 ft. area. Four cycles at 4 to 6 days each. FTEX reduced from 25 mg/L to <0.09 mg/L. property sold.
Massachusetts (1996) Injectors into GW	TCA and VC in groundwater.	H_2O_2 + Fe + acid via 2 points over 3-days within 30 ft. D.W. TCA reduced from 40.6 to 0.4 mg/L, VC 0.40 to 0.08 or ND mg/L.
Alabama (1997) Injectors into GW	Soil with high levels of TCE, DCE, and BTEX.	H_2O_2 + $FeSO_4$ via 255 injectors into 8 to 26 ft. bgs zone of clay backfill in 2 acre waste lagoons. 20 days treatment time. 72000 lbs. of NAPLs treated down to soil screening levels.
South Carolina (1997) Injectors into GW	Deep GW Zone with PCE and TCE DNAPLs in sandy clay aquifer.	H_2O_2 + $FeSO_4$ via 4 injectors into zone at 140 ft. bgs beneath old waste basin. 6-day treatment time. Treatment achieved 94% reduction in COCs with GW near MCLs. GW TCE reduced from 21 to 0.07 mg/L; PCE from 119 to 0.65 mg/L.

Table 4. Example applications of *in situ* treatment using permanganate (after USEPA 1998; Siegrist 1998)

Location (date) Delivery	Media and COCs	Application method and results
Ohio (1997) Horizontal well recirculation	Groundwater with TCE DNAPLs in a thin sandy aquifer.	$KMnO_4$ (2 to 4 wt.% feed) delivered by horizontal recirculation wells 200 ft. long and 100 ft. apart at 30 ft. bgs to treat 10^6 L zone of groundwater over 30 days. TCE reduced from 820 mg/L to MCL in 13 of 17 wells. ~300 kg of TCE destroyed. Some MnO_2 particles generated. Aquifer heterogeneities noted.
Kansas (1996) Deep soil mixing	TCE and DCE in soil and groundwater to 47ft. depth.	$KMnO_4$ (3.1 to 4.9 wt.%) delivered by deep soil mixing (8 ft. augers) to 47 ft. bgs during 4 days. TCE reduced from 800 mg/kg by 82% in the vadose zone and 69% in the saturated zone (>8 ft. bgs). MnO_4^- depleted. Microbes persisted. Comparison tests with mixed region vapor stripping yielded 69% reduction and bioaugmentation were 38% reduction.
Ohio (1998) Vertical well	TCE in silty sand and gravel groundwater zone at 30 ft. bgs.	$NaMnO_4$ (250 mg/L) delivered by 5-spot vertical well recirculation system (ctr. well and 4 perimeter wells at 45 ft. spacing) for 3 pore volumes over 10 days. TCE reduced from 2.0 mg/L to MCL. Oxidant gradually depleted in 30 d and no Microtox toxicity. No permeability loss in formation.
Ohio (1996) Hydraulic fracturing	VOCs in silty clay soil from ground level to 18 ft. bgs.	$KMnO_4$ grout delivered by hydraulic fracturing to create multi-layered redox zones. Emplaced over 4 days but sustained oxidative zone for more than 15 mon. Dissolved TCE reduced from equiv. of 4000 mg/kg by 99% during 1 hr of contact.

Table 5. Example field applications of *in situ* treatment using ozone (after USEPA 1998; Siegrist 1998)

Location (date) *Delivery*	Media and COCs	Application method and results
Colorado (1997) GW wells	Soil and GW with BTEX and TPH.	Former gas station site. Sand/gravel to 43 ft. bgs with GW at 28 ft. 3 wells to 50 ft. depth cycling air/ozone with water recirculaton. 12 cycles per day. SVE also continued. TPH in soil from 90 to 2380 mg/kg and BTEX at 7.8 to 36.5 mg/kg. TPH in GW at 490 mg/L to NAPL. After 6 mon, GW below MCLs. No soils data. System shut down.
Kansas (1997) Injectors into GW	PCE in GW.	Old drycleaners site. GW at 14 to 16 ft. bgs in terrace deposits. One sparge point at 3 scfm at 35 ft. bgs. SVE wells in vadose zone. PCE in top 15 ft. of aquifer at 0.03 to 0.60 mg/L. Reduced 91% within 10 ft. of well. Comparisons with air only indicated 66 to 87% reductions.
California (1998) Injectors into GW	Soil and GW with PAHs and PCP.	Wood treater site 300 ft. by 300 ft. in area. Stratified sands and clays. 4 multilevel ozone injectors at up to 10 cfm. SVE wells in the vadose zone. After 1 mon, PAHs at 1800 mg/kg reduced by 67 to 99% and PCP at 3300 mg/kg reduced 39 to 98%.

full-scale applications have evaluated alternative methods of oxidant delivery including permeation by vertical lances (Jerome et al. 1997), flushing by vertical and horizontal groundwater wells (Lowe et al. 1999; Schnarr et al. 1998;West et al. 1998), and reactive zone emplacement by hydraulic fracturing (Murdoch et al. 1997; Siegrist et al. 1998a,b; Siegrist et al. 1999).

Laboratory studies, field trials, and full-scale applications have generated considerable insight into the process principals and application of *in situ* chemical oxidation. In general, the oxidants have been shown to be capable of achieving high treatment efficiencies (e.g., >90%) for unsaturated aliphatic (e.g., trichloroethylene (TCE)) and aromatic compounds (e.g., benzene), with very fast reaction rates
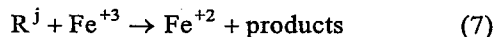
(90% destruction in minutes). Field applications have demonstrated very high reductions in the mass of contaminants, but only where adequate oxidant was able to be delivered and contacted with the target organics. These field applications have been particularly valuable in that they have clearly affirmed the control that field-scale reaction and transport processes exert on design and performance of *in situ* chemical oxidation.

Oxidants and Reaction Chemistry

Studies of the peroxide degradation of toxic organics in soil and groundwater initially focused on petrochemicals (e.g., naphthalene, phenanthrene, pyrene and phenols) but later work encompassed chlorinated solvents (e.g.,

TCE, tetrachloroethylene (PCE)) (Watts et al. 1990; Watts and Smith 1991; Watts et al. 1991; Tyre et al. 1991; Ravikumar and Gurol 1994; Gates and Siegrist 1993; 1995; Watts et al. 1997). Oxidation using H_2O_2 in the presence of native or supplemental Fe^{+2} produces Fenton's reagent, which yields free radicals (OH^j) that can rapidly degrade a variety of organic compounds (Table 1).

However, the application of peroxide to soil and ground-water systems involves a variety of competing reactions as follows:

$$H_2O_2 + Fe^{+2} \rightarrow OH^{-\alpha} + Fe^{+3} + OH^* \quad (1)$$

$$H_2O_2 + Fe^{+3} \rightarrow HO_2^* + H^+ + Fe^{+2} \quad (2)$$

$$OH^* + Fe^{+2} \rightarrow OH^- + Fe^{+3} \quad (3)$$

$$HO_2 * + Fe^{+3} \rightarrow O_2 + H^+ + Fe^{+2} \quad (4)$$

$$H_2O_2 + OH^j \rightarrow H_2O + HO_2^* \quad (5)$$

$$RH + OH^j \rightarrow H_2O + R^* \quad (6)$$

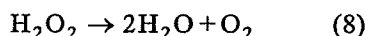$$R^j + Fe^{+3} \rightarrow Fe^{+2} + products \quad (7)$$
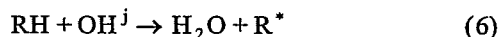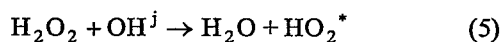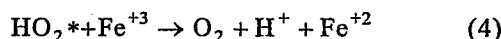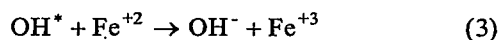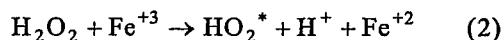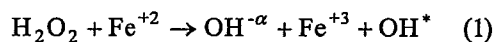
Hydrogen peroxide can also autodecompose in aqueous solutions with accelerated rates upon contact with mineral surfaces as well as carbonate and bicarbonate (Hoigne and Bador 1983) (eqn. 8).

$$H_2O_2 \rightarrow 2H_2O + O_2 \quad (8)$$

The simplified stoichiometric reaction for peroxide degradation of TCE is shown in eqn. 9.

$$3H_2O_2 + C_2HCl_3 \rightarrow 2CO_2 + 2H_2O + 3HCl \quad (9)$$
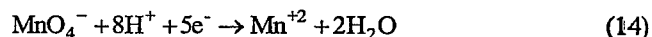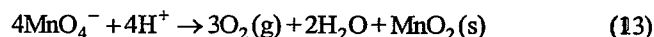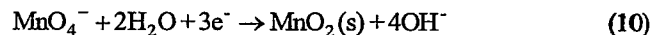
Fenton's Reagent oxidation is most effective under very acidic pH (e.g., pH 2 to 4) and becomes ineffective under moderate to strongly alkaline conditions and/or where free radical scavengers are present (e.g., CO_3^{-2}). The reaction is strongly exothermic and can evolve substantial gas and heat. The oxidative reactions are extremely rapid and follow second-order kinetics (see following section).

For application *in situ*, there are three processes that have been patented based on reaction chemistry and/or mode of delivery: CleanOX, GeoCleanse, and ISOTEC methods. While the specifics of an application to a given site will be very site dependent, *in situ* chemical oxidation with peroxides has typically included H_2O_2 concentrations in the range of 5 to 50 wt.% and where native iron has been lacking or unavailable, ferrous sulfate is often added at mM levels. In some cases acetic or sulfuric acids are also added to reduce the pH to a more favorable acidic range. Delivery methods have included common groundwater wells or specialized injectors. In many cases, multiple doses or application cycles are used to facilitate more uniform delivery of reagents and efficiency of treatment.

Compared to peroxide, permanganate oxidation of soil and groundwater has more recently been studied for *in situ*

treatment of chlorinated solvents (e.g., TCE, PCE) and petrochemicals (e.g., naphthalene, phenanthrene, pyrene and phenols) (Vella et al. 1990; Leung et al. 1992; Vella and Veronda 1994; Gates et al. 1995; Yan and Schwartz 1996; Schnarr et al. 1998; West et al. 1998a,b; Siegrist et al. 1998a,b; Lowe et al. 1999; Siegrist et al. 1999; Struse 1999). The reaction stoichiometry and kinetics in natural systems are quite complex and are as yet not yet fully understood. Permanganate (typically as $KMnO_4$ but also available in Na, Ca, or Mg salts) can participate in several reactions as determined to a large degree by system pH. For example, between a pH of 3.5 and 12, permanganate ion reacts slowly, but observably, to form manganese dioxide (eqn. 10). Above a pH of about 12, manganate ions (Mn (VI)) may be formed (eqn. 11). Hydroxyl radicals may also be formed in alkaline solutions (eqn.12). In slightly acidic solutions, the permanganate ion can decompose slowly to form manganese dioxide with a release of oxygen (eqn.13). Below a pH of about 3.5, Mn(II) cations are formed (eqn.14). Under acidic conditions, the permanganate ion can then oxidize the Mn(II) to form manganese dioxide (eqn.15).

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2(s) + 4OH^- \quad (10)$$

$$MnO_4^- + H_2O \rightarrow MnO_4^{-2} \quad (11)$$

$$MnO_4^- + H_2O \rightarrow MnO_4^{-2} + OH^* + H^+ \quad (12)$$

$$4MnO_4^- + 4H^+ \rightarrow 3O_2(g) + 2H_2O + MnO_2(s) \quad (13)$$

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{+2} + 2H_2O \quad (14)$$

$$2MnO_4^- + 3Mn^{+2} + 2H_2O \rightarrow 5MnO_2(s) + 4H^+ \quad (15)$$

The stoichiometric reaction for the complete destruction of TCE by $KMnO_4$ is given in equation 16.

$$2KMnO_4 + C_2HCl_3 \rightarrow 2CO_2 + 2MnO_2 + 2KCl + HCl \quad (16)$$
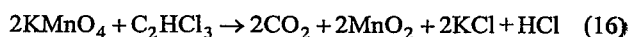
Under neutral or acidic pH, oxidation is speculated to occur through the formation of a cyclic ester with further reaction yielding organic acids and aldehydes as well as CO_2 and $MnO_{2(s)}$ (eqn.16) (Arndt 1981; Leung et al. 1992; Yan and Schwartz 1996). Halogenated substitution with Cl^- may facilitate C-C cleavage during oxidation, although the rate of reaction slows with increasing Cl^- substitution (Yan and Schwartz 1996). For example PCE degradation is slower than TCE. The reaction appears to be 2nd-order with a rate constant of ~0.6 L $mol^{-1}s^{-1}$ (in clean groundwater). Solution pH between 4 and 8 has little or no effect on rate, but temperature does effect the rate as described by the Arhenius equation (Case 1997). In alkaline solutions, hydroxyl radicals may also be formed which can contribute to oxidative destruction (eqn.12). The reaction can include destruction by direct electron transfer or free radical advanced oxidation. The pH of the reacting system can decline to strongly acidic conditions (e.g., pH 2 to 3) depending on the buffering capacity of the system. Key reaction products can include intermediate organic acids along with production of manganese oxide solids and chlorides.

Ozone gas has been injected into the subsurface along with air sparging to remediate organics in groundwater zones (Bellamy et al. 1991, Nelson and Brown 1994, Marvin et al. 1998). Ozone can oxidize contaminants directly or form OH^i radicals, strong nonspecific oxidants. Contaminants oxidizable by ozone include aromatics, PAHs, chloroethenes, pesticides and aliphatic hydrocarbons. The simplified stoichiometric reaction of ozone with TCE in water is given by eqn. 17.

$$O_3 + H_2O + C_2HCl_3 \rightarrow 2CO_2 + 3HCl \quad (17)$$
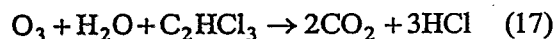
The oxidation reaction can be described as a pseudo-1st order reaction with extremely fast kinetics. Due to ozone's high reactivity and instability, O_3 is produced onsite by electrical generators. In addition, the high reactivity of ozone and free radicals requires relatively closely spaced delivery points (e.g., air sparging wells). In some settings, scavengers for OH^i can reduce the reaction efficiency. Gas and heat can be evolved and in fine-grained sediments, particulates can conceivably be generated. Decomposition of the ozone can lead to beneficial oxygenation and biostimulation.

Kinetics of Reaction and Delivery Methods

Pseudo 1st- or 2nd-order kinetic models often describe the kinetics of reaction of oxidants with target organics of concern. For example during the past year, kinetic studies have been completed for treatment of TCE over a wide range of concentrations (0.5 to 800 mg/L) in simulated and site groundwaters using permanganate solutions or solids at stoichiometric dosages in the range of 5x to 10x. The reaction order and kinetic parameters have been examined using pseudo 1st and 2nd-order kinetic models fit to the data:

$$1^{st} - \text{order} \quad d[C_1]/dt = -k_1[C_1] \quad (18)$$

$$2^{nd} - \text{order} \quad d[C_1]/dt = -k_2[C_1][C_2] \quad (19)$$

$$\text{Pseudo}1^{st} - \text{order} \quad d[C_1]/dt = -k'[C_1]$$

$$k' = k_2[C_2] \quad (20) \text{and} (21)$$

where, $d[C_1]/dt$ = rate of change in concentration of the target compound ($ML^{-3}T^{-1}$), k_1 = 1st-order rate constant (T^{-1}), $[C_1]$ = concentration of the target compound (ML^{-3}), k_2 = 2nd-order rate constant ($L^3M^{-1}T^{-1}$), $[C_2]$ = concentration of the oxidant (ML^{-3}), and k' = pseudo 1st-order rate constant (T^{-1}). With respect to TCE degradation by $KMnO_4$ (in the absence of natural organic matter (NOM)), the reaction is clearly 2nd-order (eqn. 19). A recent study by the authors with a range of TCE and $KMnO_4$ conditions (0.6 to 6.3 mM) yielded an average k_2 of 0.9 L mol^{-1}s^{-1} with a %R.E. of only 12%.

The kinetics of oxidation of a given target organic chemical are also affected by matrix conditions, most notably, temperature and the concentration of other oxidant demanding substances such as natural organic matter

(NOM). Temperature effects can be described by the Arhenius equation (Case 1997). However, the effects of NOM (or minerals) on the oxidant demand rate and extent is not clearly understood. Limited research suggests that the rate of oxidant consumption is comparable or slower than that of most target chemicals and that only a fraction of the total NOM is susceptible to oxidation. It is clear however that the rate and extent of demand must be accounted for or a kinetic model, such as equation 19, will grossly over predict the rate of destruction of a target like TCE. Moreover, if the NOM demand is too high, it will deplete the oxidant and cause the reaction with the target organic to cease altogether.

Another factor affecting the kinetics of destruction is the phase of the target organic contaminant of concern (i.e., whether the organic is in the dissolved, sorbed, or nonaqueous liquid phase). Most research has been conducted with dissolved phase organics. Limited research with Fenton's reagent (Tyre et al. 1991, Li et al. 1997, Watts et al. 1997) and permanganate (unpublished CSM work), suggests that sorption is not rate limiting under the usual high oxidant doses and energetic reaction conditions. In addition, research on the oxidative destruction of nonaqueous phase liquids is limited but preliminary results by Urynowicz at CSM revealed that the rate of pure phase dissolution and degradation is accelerated by permanganate in the bulk solution (unpublished CSM work).

Given the relatively indiscriminate and rapid rate of reaction of the oxidants with reduced substances for all oxidants, as well as autodecomposition of peroxide, the method of delivery and distribution throughout a subsurface region of interest is of paramount importance. Oxidant delivery systems often employ vertical or horizontal wells with forced advection to rapidly move the oxidant away from the initial point of entry into the subsurface (Figure 2, Tables 3 to 5). Alternatively, oxidant delivery systems can employ vertical lance injection or sparging systems that enable high density delivery to minimize transport distances and enhance contact with target chemicals. In contrast to peroxide and ozone oxidants, permanganate is less prone to decomposition and is more stable and as a result, it can migrate by diffusive processes albeit at slow rates of transport (Struse 1999).

Design and Implementation

The standard-of-practice for the design and implementation of in situ chemical oxidation technologies is still evolving. While there have been numerous laboratory studies and an increasing number of field-scale trials and full-scale projects, there are still gaps in the current knowledge base and performance deficiencies have been observed. Engineering of in situ oxidation technologies must therefore be done carefully with due attention to both reaction chemistry as well as delivery and transport processes. Figure 2 provides the conceptual design process that these authors have developed and utilized during the past three years. The design and implementation process should rely
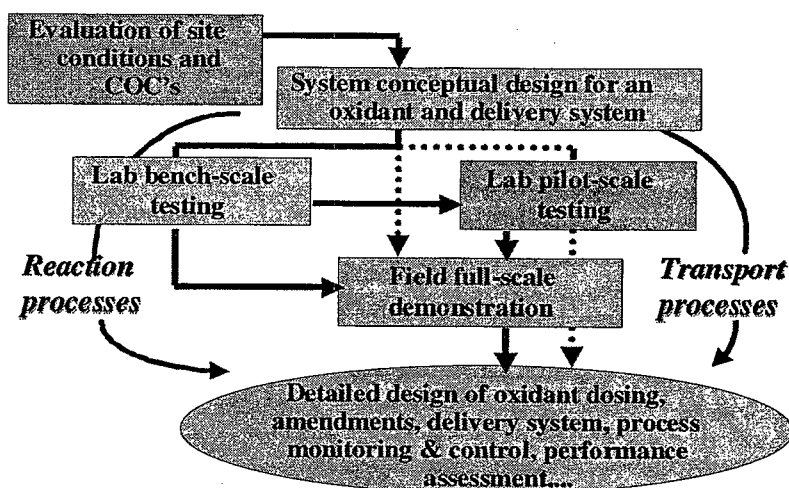
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Figure 2. Process design approach for *in situ* chemical oxidation.

on an integrated effort involving screening level characterization tests and reaction and transport modeling, combined with treatability studies at the lab and field scale.

Past experience and consideration of the current state-of-knowledge suggest there are some key issues that must be carefully considered during design process. These include: (1) oxidant suitability to degrade the target chemicals at the rate and to the level required under given environmental matrix conditions, (2) rate and extent of natural oxidant demand, (3) viability of and method for oxidant delivery throughout the subsurface region of interest, (4) potential for oxidation-induced adverse secondary effects (e.g. toxic byproduct formation, gas evolution, impurities in the oxidant, particle genesis and permeability loss, mobilization of metals), and (5) compatibility of oxidation with other technologies (e.g., natural attenuation) and post-treatment land use. The relevance of these issues and the need for their accurate and complete delineation during system design is highly dependent on the site specific conditions and context of the application being contemplated.

Conclusions

In situ chemical oxidation is rapidly emerging as a viable remediation technology for mass reduction in source areas as well as for plume treatment. The oxidants most commonly employed to date include peroxide, permanganate and ozone systems, with subsurface delivery to groundwater by vertical or horizontal wells and sparge points and to soil by lance injectors and hydraulic fracturing. The potential benefits of *in situ* oxidation include the rapid and extensive reactions with various COCs, applicable to many biorecaciltrant organics and subsurface environments, can be tailored to a site from locally available components and resources, and can facilitate property transfers and Brownfields development projects. Some

potential limitations exist including, requirement for handling of large quantities of hazardous chemicals to be introduced due to the oxidant demand of the target organics and the unproductive oxidant consumption of the formation, some COCs are resistant to oxidation, and there is a potential for process-induced detrimental effects including gas evolution, permeability loss, and mobilizing redox sensitive and exchangeable sorbed metals. Full-scale deployment is accelerating, but care must be taken to avoid poor performance and unforeseen adverse effects. Matching the *oxidant and delivery system* to the *COCs and site conditions* is the key to achieving performance goals. Further development work is ongoing in many areas.

Acknowledgments

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Fenton Oxidation, Carbon Regeneration, and Groundwater Remediation

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Abstract

A ground water treatment process is described in which contaminants are adsorbed onto granulated activated carbon (GAC) containing fixed iron oxide. Hydrogen peroxide (H_2O_2) is amended to the GAC suspension and reacts with the iron, forming hydroxyl radicals ($\cdot OH$). The radicals react with and oxidize sorbed and soluble contaminants regenerating the carbon surface. Laboratory results are presented in which 2-chlorophenol (2CP) was first adsorbed to GAC and subsequently oxidized via the Fenton-driven mechanism. Transformation of 2CP was indicated by the formation of carboxylic acids and Cl^- release. 2CP treatment efficiency, defined as the molar ratio of Cl^- released to H_2O_2 consumed, increased with increasing amounts of iron oxide and 2CP on the GAC. The extent of 2CP oxidation increased with H_2O_2 concentration. Lower treatment efficiency was evident at the highest H_2O_2 concentration utilized (2.1 M) and was attributed to increased $\cdot OH$ scavenging by H_2O_2. Aggressive oxidation procedures used in sequential adsorption/oxidation cycles did not alter the GAC surface to a degree that significantly interfered with subsequent 2CP adsorption reactions. Although process feasibility has not yet been established beyond bench-scale, experimental results illustrate the potential utility of the adsorption/oxidation process in above-ground systems or permeable reactive barriers for the treatment of contaminated ground water.

In Situ Chemical Oxidation for Groundwater Remediation Near a Waste Injection Well

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In situ chemical oxidation (ISCO) is being evaluated for potential use in remediating groundwater contamination near a former waste disposal well in a fractured basalt aquifer. The site is Test Area North (TAN), a facility at the Idaho National Engineering and Environmental Laboratory (INEEL), a U.S. Department of Energy laboratory in southeastern Idaho.

The TAN facility is underlain by a sequence of plains-type basalt flows intercalated with eolian and alluvial sedimentary interbeds that were deposited between volcanic eruptions. Individual basalt flows average about 20 feet in vertical thickness. Basalt flows have a typical morphology controlled by its cooling history. The interior of a typical flow is massive, while the upper and lower portions are highly fractured, vesicular, and scoriaceous. Hence, flow interiors tend to have relatively low permeability while the interflow zones (the area at the top of one flow and the bottom of the overlying flow) have relatively high permeability. On a local scale the spatial distribution of permeable units is highly complex due to the complex morphology of coalescing basalt flows. On a larger scale, the highly permeable zones are sub-horizontal features that can be correlated between well pairs. Sedimentary interbeds are typically low permeability units that, where laterally extensive, restrict vertical movement of water and solutes through the system. The water table at TAN lies approximately 200 feet below ground surface. A laterally extensive, fine-grained interbed at a depth of approximately 400 feet below ground surface provides a base to the contaminated upper portion of the aquifer beneath TAN.

Test Area North was developed during the early 1950s for conducting research on nuclear power reactors, including nuclear powered aircraft. Between 1953 and 1972, liquid wastes were disposed by injecting them into the upper portion (200 to 300 feet below grade) of the Eastern Snake River Plain aquifer using injection well TSF-05. The wastes included sanitary sewage, wastes from manufacturing, machining, and maintenance activities, and from nuclear reactor research. The injected wastes included tetrachloroethene (PCE) and trichloroethene (TCE), and radionuclides. Wastes apparently received little treatment other than grinding prior to disposal. The wastes included a solid fraction. This sludge accumulated in the well and reduced the permeability of the formation, which contributed to a decision to discontinue use of the well for waste injection. The remnants of this sewage sludge is still present in the formation, and is referred to as 'organic sludge'.

Groundwater contamination at TAN was discovered during routine monitoring of water supply wells at TAN in 1987, when PCE and TCE were detected. Subsequent investigations performed during a CERCLA remedial investigation and afterwards revealed that a TCE plume extends approximately 10,000 feet downgradient from TSF-05. There are smaller plumes of PCE and other chloroethenes. Tritium is pervasive at sub-MCL concentrations throughout the TCE plume, while ^{90}Sr, ^{137}Cs, and ^{234}U are present above risk-based concentrations in limited areas near the former injection well. TCE is the compound of greatest interest due to the large areal extent of the TCE plume. The TCE plume appears to have been stable for the last ten years. The highest contaminant concentrations are found today - 27 years after waste injection ceased - in the immediate vicinity of the injection well. Coupled with several lines of evidence that show that organic sludge is still present in the formation, this indicates that there is a secondary contaminant source that continues to leach dissolved contaminants into groundwater.

The secondary source includes several components. Organic sludge, which would be a good sorbent for chloroethenes due to its high organic carbon content, is known to be present in the formation near the injection well. Although it has not been directly observed, non-aqueous phase liquid may be present, as suggested by per-

cent range concentrations of chloroethenes in sludge samples recovered from the injection well. Finally, dissolved contaminants may have diffused into matrix porewater.

In 1995, a record of decision (ROD) was signed that specifies the remedial actions for contaminated groundwater beneath TAN. The ROD specifies that pump-and-treat (P&T) will be used to prevent migration of contaminants in groundwater that emanates from the hot spot near the injection well, and also specifies that a separate P&T system will be used for extracting dissolved contaminants from the plume downgradient of the hot spot. The parties to the ROD recognized that P&T has a poor track record for returning aquifers to pristine conditions, and hence also stipulated that several alternative technologies be evaluated for possible use in enhancing or replacing one or both P&T systems. *In situ* chemical oxidation was identified in the ROD as a technology that may be applicable for remediating the hot spot, and hence a treatability study of ISCO is being conducted.

The objective of ISCO for long term application at the hot spot is to prevent migration of chloroethenes at concentrations above MCLs in groundwater that emanates from the hot spot. The approach would be to destroy enough of the secondary source that mass transfer of contaminants from the secondary source into groundwater would be substantially reduced, such that dissolved concentrations in groundwater would be less than MCLs. The goal of the ISCO treatability study, which is currently in progress, is to determine the feasibility of using ISCO for hot spot remediation. The specific objectives are to evaluate the effectiveness of ISCO for reducing mass transfer from the secondary source, and to evaluate possible long term effects of ISCO other than secondary source destruction.

Based on previous work, potassium permanganate was selected as the oxidant to be evaluated in the treatability study. It was selected largely because it is a strong oxidant, it is readily available, and it is easy to use under field conditions. The reaction of potassium permanganate with TCE is represented by

$$C_2CL_3H + 2KMnO_4 + 2H_2O \rightarrow$$

$$2MnO_{2(s)} + 3H^+ + 2HCO_3^- + 2K^+ + 3Cl^-$$
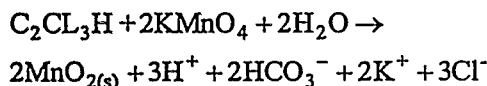
A laboratory treatability study was performed for the INEEL by the Oak Ridge National Laboratory. The objectives of this study were to measure the amount of oxidant consumed (oxidant demand) by reaction with geologic materials and with anthropogenic wastes, and to measure the rate of chloroethene oxidation as a function of oxidant and chloroethene concentration. The oxidant demand of geologic materials was found to be small (~0.1 g MnO_4^- /kg), while the oxidant demand of organic sludge was much higher (70 g MnO_4^-/kg). Oxidation destroyed the organic carbon fraction of organic sludge, thereby removing most of the ability of the sludge to sorb chloroethenes.

TCE was rapidly oxidized in the lab experiments, which were performed in sealed, gently agitated, batch reactors. Initial concentrations of permanganate ranged from 0.01% to 3%. TCE concentrations typically declined from the initial concentration (0.1 to 1000 mg/L) to the MDL (5 to 10 mg/L) when the first (1/2 hour) or second (2 hours) samples were collected. The data resolution was usually not sufficient to allow calculation of a first order rate constant, and thus the lower bound of a zero order rate constant was calculated. These rates are >0.1 to >4000 mg TCE L^{-1} h^{-1}. Even the slowest reaction rates are fast relative to the time scale at which ISCO would be applied at the field scale, which would have contact times of days or longer. TCE added as a NAPL to some batch reactors was rapidly destroyed. It is thought that oxidation in the aqueous phase maintained very low dissolved concentrations, which enhanced the rate of mass transfer from the NAPL into the aqueous phase. Thus, although TCE is not oxidized in the non-aqueous phase, the net effect of oxidation was to reduce the mass of non-aqueous phase TCE.

The lab study results suggest that the chemical reaction aspects of ISCO are feasible, that oxidation destroys TCE in each of the secondary source forms thought to be present at TAN, and that the loss of oxidant to unproductive reactions with geologic material are not exorbitant. Hence, a field evaluation is being planned for the 2000 field season.

The objectives of the ISCO field evaluation are to evaluate the effectiveness of ISCO for reducing the concentrations of dissolved chloroethenes in and downgradient of the hot spot, and to evaluate the effects of ISCO other than secondary source destruction. The potential secondary effects include introduction of heavy metals into the aquifer, and mobilization of previously injected contaminants. Industrial grade potassium permanganate contains heavy metals as minor constituents, and if sufficiently high permanganate concentrations are used the MCLs for these metals could be exceeded in the oxidant solution. Radionuclides (^{90}Sr and ^{137}Cs) that were previously disposed are now immobilized in the hot spot. The effect of ISCO on the mobility of these contaminants will be investigated.

The approach to be utilized in the field evaluation is to make a series of oxidant solution injections into the former injection well (TSF-05), and then to assess the effect of oxidation on VOC mass transfer from the secondary source into groundwater. This cycle of oxidation - performance assessment will be repeated several times.

Oxidant solution will be injected using the single well push pull test (SWPPT) approach, in which both permanganate and a conservative tracer (bromide) will be injected, allowed to react, and then extracted. The recovery of oxidant relative to bromide can be used to deduce reaction rates and the mass of oxidant consumed by reactions in the subsurface. A series of SWPPTs will be performed.

The trend of oxidant demand (in a single test) as a function of the cumulative amount of oxidant injected will be used to infer whether ISCO is having a significant effect on the mass of oxidizable material (assumed to be predominantly organic sludge) in the hot spot.

The effect of ISCO on mass transfer from the secondary source will be periodically assessed by injecting VOC-free potable water into the aquifer, and monitoring VOC concentration rebound afterwards. Previous studies at TAN have shown that VOC concentrations rise following injection of VOC-free water, presumably due to mass transfer from the secondary source. Differences in pre-ISCO to post-ISCO rebound behavior should reflect differences in mass transfer from the secondary source, and hence be a direct measurement of the effect ISCO on the secondary source.

In summary, laboratory studies suggest that the chemical aspects of ISCO are favorable for remediating the secondary source of contamination in the aquifer near a former waste injection well at Test Area North. A field evaluation that will address the effectiveness of ISCO under field conditions is planned.

Groundwater Remediation Using the CleanOX *In Situ* Chemical Oxidation Process

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In 1998, ManTech acquired the assets of CleanOX Environmental Services, Inc. of Houston, Texas including the equipment, personnel, and patents for implementation of the CleanOX Process. CleanOX is a patented technology that is applicable for *in situ* remediation of organic contamination in groundwater and saturated soils, including fuels, solvents, and pesticides. The CleanOX Process reduces groundwater contaminants to harmless carbon dioxide and water through an injection method that costs significantly less than conventional environmental remediation technologies. Since 1993, this innovative technology has been successfully used on scores of sites in the United States.

The CleanOX Process oxidizes hydrocarbon and other organic contamination in groundwater and saturated soil using Fenton's Reagent. The CleanOX technology is an *in situ* process utilizing the injection of proprietary liquid chemical formulations that generate hydroxyl radicals, via a Fenton Reaction, in the subsurface. The reagents are applied to the subsurface through wells that are installed within the contaminated portion of an aquifer. The reagents are formulated based on site-specific conditions, but typically include acids, catalysts, and peroxide. Prior applications of the process have demonstrated immediate reductions in the concentrations of the following constituents:

- Aromatic Compounds (BTEX)
- Total Petroleum Hydrocarbons (TPHs)
- Chlorinated Solvents
- Polynuclear Aromatic Hydrocarbons (PAHs)
- Nitro-aromatic Compounds
- Organic Pesticides
- Alcohols (phenols)
- Mineral Oil Products
- Polychlorinated Biphenyls (pcbs)

The CleanOX Process has been developed over the last 7 years for the remediation of organic contaminants in groundwater, saturated soil and contamination within a natural attenuation solution is viable, and to rapidly remediate sites that are part of a real estate transfer or brownfield project.

Key Advantages for applying the CleanOX Process include:

- Contaminant reduction in weeks to months;
- Mobile *in situ* treatment system that has limited disruption to on-site operations;
- CleanOX reagents applied to two-inch diameter monitoring wells;
- Applied under buildings and within operational areas;
- Requires no capital equipment purchase; and
- Eliminates long-term operation and maintenance (O&M) costs.

The CleanOX Process is applied in a phased program:

- Bench test to determine the effectiveness of CleanOX reagents;
- Field pilot test performed within source area to reduce contaminant concentrations and obtain data for full-scale application; and
- Full-scale remediation of groundwater plume to reduce or eliminate organic contamination.

The CleanOX technology has been applied at over 80 sites within the United States including Superfund sites, Fortune 500 industrial sites, commercial retail properties, gasoline service stations, land disposal facilities, DoD installations, and dry cleaners.

Field applications usually require one to two weeks on-site, with the chemical reactions being complete 48 hours after application. Groundwater can be sampled from weeks to months after the CleanOX application.

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CleanOX Process Chemistry

The basis of the CleanOX Process chemistry is related to the well-known Fenton's Reaction wherein hydrogen peroxide reacts with a ferrous ion to produce an hydroxyl radical in the acidified aqueous medium containing the contaminants(s) according to the equation:

$$H_2O_2 + Fe^{+2} \xrightarrow{\text{acid}} OH\bullet + OH^- + Fe^{+3}$$
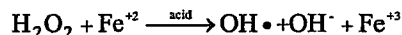
The hydroxyl free radical OH$ is an extremely powerful oxidizer which progressively reacts with organic contaminants yielding carbon dioxide and water. The basic oxidation reaction (without inhibitor, initiator, enhancer, or catalytic chemistry included) is:
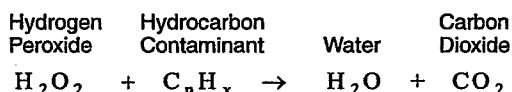
Hydrogen Peroxide	Hydrocarbon Contaminant		Water	Carbon Dioxide
H_2O_2	$+\ C_nH_x$	$\rightarrow$	H_2O	$+\ CO_2$

This chemical form of the CleanOX Process indicates the environmental compatibility of the technology. Laboratory test data from post-treated groundwater grab samples has not indicated the generation of harmful chemical bi-products from the application of the process. Some transitory pH shift toward acidic occurs during treatment; however, the acidic groundwater will equalize over time.

The oxidation process generates progressively shorter chemical chains, cleaving chemical bonds, and eventually resulting in carbon dioxide and water. A proprietary, empirically-derived computer modeling program developed from laboratory and field applications over the last several years, Geo-Environmental Modeling Software (GEMS), is used to design each process application. GEMS generates a custom, site-specific treatment design and dosage for the application of the process from the relevant quantified engineering parameters and the hydrogeology, water chemistry, and contaminants at a given site.

The design and treatment cost will depend upon the site-specific parameters including contaminant concentration, groundwater flow rate, porosity and permeability of subsurface soil, and the vertical and lateral extent of contamination. The CleanOX Process is primarily directed toward remediating dissolved-phase and adsorbed-phase organic contamination, but has been applied to treat free-product phases and capillary fringe soils. CleanOX can be applied for augmentation of existing treatment technologies such as pump and treat, air sparging, and other remediation methods.

CleanOX Process Field Application

The field application of the CleanOX Process includes the following elements:

- installation of application wells of similar construction as monitoring wells;

- performing sampling and analyses of soil and/or groundwater samples within the treatment area to establish baseline contaminant concentration conditions;

- mobilization of reagents and field technicians to the site;

- attaching well head apparatus and chemical feed lines to each application well;

- application of the site-specific reagent dosage to each application well;

- field monitoring of groundwater and application well parameters during reagent injection to ensure safety, efficiency, and effectiveness of the process;

- performing sampling and analyses of soil and/or groundwater within one month following application to determine application effectiveness; and

- completing additional rounds of reagent application, as needed, to effect further contaminant concentration reductions.

There are several critical elements that contribute to the success of a in situ chemical oxidation application. The most important element is safety. The application of Fenton's Reaction chemistry to the subsurface environment results in vigorous, exothermic, pressurized subsurface environment. CleanOX applications are designed and implemented so that the reagents are applied in a controlled, conservative manner to avoid dangerous pressurization and runaway reactions. Another important factor that contributes both to safety and effectiveness is peroxide delivery rate and concentration. Again, our initial designs for a given site are based on observations made during the laboratory bench-scale testing of site soil and groundwater and on the output of the GEMS model. These design formulations of reagent concentration and delivery rate are never immediately applied at a site. ManTech personnel begin peroxide application at a site with a slow flow rate of dilute reagents until monitoring of the subsurface confirms that hydroxyl radical formation reaction and subsequent oxidation reactions have initiated and are at steady-state. Reagent concentrations and delivery rates are then slowly increased until design parameters are achieved.

CleanOX Case Studies
Light, Non-Aqueous-Phase Liquids at a DOD Fuel Farm in Puerto Rico

The CleanOX in situ chemical oxidation process was applied at an active military fuel farm for remediation of light, non-aqueous-phase liquids (LNAPL) detected at the site. Soil and groundwater impacts from petroleum product releases (jet fuel and diesel) had been studied for several years at the site under RCRA requirements. ManTech was contracted by the prime consultant to conduct a pilot test at the site to determine the applicability, feasibility, effectiveness, and cost to address the LNAPL as a full-scale remedial action at the site. Results of the pilot test will be included in the prime consultant's corrective measures study (CMS).

The facility is located in Puerto Rico and has been operated by the DoD since the early 1950s. A combination of fuel tank leaks, piping leaks, overfills, spills, and past maintenance practices has resulted in contaminated surface and subsurface soil and groundwater at the site. DoD is currently preparing an evaluation of remediation alternatives that will meet USEPA and Puerto Rico regulatory requirements. Cleanup of the LNAPL impacted areas at the site by mechanical pumping (skimming) has been projected to take as long as 60 to over 100 years due to the low hydraulic conductivity of the site soils (10^{-4} to 10^{-5} cm/sec) which originated from weathered volcanic bedrock.

ManTech conducted a bench test of the CleanOX Process on groundwater and free product samples provided by the prime contractor and prepared a Work Plan for implementing a pilot test of the CleanOX Process. The Work Plan provided detailed information regarding our understanding of the site conditions and the results of the bench test. The Work Plan was presented to the prime contractor, DoD, the USEPA, and the Puerto Rico Environmental Quality Board (EQB) in order to obtain regulatory approval and to negotiate the pre- and post-treatment monitoring requirements. Further, the Work Plan detailed the various DoD requirements and plans needed for the project (e.g. spill control, environmental protection, quality assurance, etc.).

The pilot test consisted of installing two, two-inch diameter stainless-steel application wells and four, two-inch diameter PVC monitoring wells; collecting pre-and post-treatment site data; and applying CleanOX Process reagents to degrade LNAPL. The pilot test wells were installed in an upgradient area of the LNAPL plume where LNAPL measurements varied from several inches to several feet thick in two existing monitoring wells. ManTech collected baseline soil and groundwater samples to establish the initial contaminant mass loading adsorbed to site soils, dissolved in site groundwater, and as a separate phase LNAPL. CleanOX Process reagents were applied over a two week period while monitoring field-measured parameters such as dissolved oxygen, oxidation-reduction potential, pH, temperature, specific conductance, and LNAPL thickness. No measurable LNAPL was detected in either the off-set monitoring wells (located 12 to 15 feet from application wells) or the application wells by the conclusion of the pilot test.

Following the reagent application phase of the pilot test, ManTech conducted a one-week, three-week, and 60-day post-treatment monitoring program. No measurable LNAPL was detected in any of the application or monitoring wells during the one-week and three-week monitoring events. Due to the size of the LNAPL plume, re-infiltration of LNAPL was observed at the 60 day monitoring event when LNAPL was measured at one to two inches in outlying monitoring wells. Contaminant mass balance calculations, based on soil and groundwater analyses and on LNAPL measurements, indicated that as much as 1,000 pound of petroleum product was oxidized during the pilot

test. Pilot test data are being compiled to estimate the scope and cost of full-scale remediation of the site.

Light Non-Aqueous-Phase Liquids at an Abandoned Industrial Facility: Boston, Massachusetts

The CleanOX *in situ* chemical oxidation process was applied at an abandoned facility for remediation of light, non-aqueous-phase liquids (LNAPL) detected at the site. The former industrial facility was undergoing redevelopment by a property developer, and LNAPL removal was required to keep the redevelopment schedule on-track. ManTech was contracted by the developer to address the LNAPL as an interim remedial measure. Only four months were required to complete the project, from the time ManTech was first contacted through the completion of the field application of the CleanOX process.

LNAPL was encountered during removal of the underground storage tank (UST) used to store no. 2 fuel oil. The UST was located outside the boiler room wall and subsequent assessment activities showed that the LNAPL had migrated under the building foundation. The LNAPL plume was estimated at approximately 2,000 square feet. LNAPL thickness was highest at the former tank bed at 1.5 feet and was measured at 2 to 4 inches over the rest of the impacted area. The geology underlying the site was characterized as fine-grained sand with lenses of silty, fine sand and silt, and trace clay. The hydraulic conductivity of subsurface soil was estimated using slug tests at 3.5×10^{-5} cm/sec. Regionally, bedrock exists at an estimated depth of 50 to 100 feet below ground surface (bgs). The depth to groundwater at the site was measured at approximately 20 feet bgs. Further, the basement of the on-site building was approximately 15 feet below grade, making the depth to groundwater under the building five feet.

Based on the geology of the site and the results of bench testing, seven application wells were used during the course the project. ManTech mobilized to the site with materials and equipment to apply one cycle of treatment to all six wells over a two week period. Monitoring during the application indicated that oxidation-reduction potential (ORP) and dissolved oxygen levels increased significantly in treatment area monitoring wells.

LNAPL measurements were made over a two-week stabilization period. Most wells were found to have a slight sheen of LNAPL, and the tank bed well had less than one foot of LNAPL. A second cycle of CleanOX treatment was implemented focusing more on the tank bed area where LNAPL thickness was the greatest. Monitoring that was performed following the second application cycle indicated that no measurable product was detected in any of the site wells. Groundwater sampling and analysis was then conducted for use in risk analysis. Based on the risk analysis results, the site owner will either apply for site closure or may perform additional CleanOX process application cycles as a polishing step to achieve site closure.

Chlorinated Hydrocarbons at a Former Manufacturing Facility in Arkansas

A CleanOX *in situ* chemical oxidation project was conducted at a former manufacturing facility in Arkansas to demonstrate that the process could rapidly degrade hydrocarbon contamination in groundwater and saturated soil underlying the plant site. The perched water table had been contaminated with chlorinated hydrocarbons from previous material handling practices associated with chlorinated solvents including trichlorethylene (TCE) and 1,2- dichloroethylene (1,2-DCE).

After a successful bench test, the CleanOX Process was applied using two on-site groundwater monitoring wells. These application wells were selected where the highest concentration of chlorinated solvents had been detected on-site. During the application of the CleanOX reagents, elevated photoionization (PID) readings were not observed during monitoring of the on-site wells. Post-application head space monitoring determined that the vapor concentrations in the on-site monitoring wells had been reduced.

Analysis of groundwater samples following application of the CleanOX Process indicated a 93% to 97% reduction of the chlorinated solvent constituents in the two demonstration wells. Based on this dramatic reduction in contaminant concentration and the absence of environmental or human receptors, the site owner petitioned for closure pending the results of the on-going groundwater monitoring program.

Volatile Organic Compounds (ug/L)	Pre-Pilot Study		Post-Pilot (7 days)		Post-Pilot (56 days)	
	MW-15	MW-108	MW-15	MW-108	MW-15	MW-108
Trichloroethene	20,000	1,100	2,900	9,500	1,700	<10
1,2-Dichloroethene	11,000	340	1,600	35	540	<10
Vinyl Chloride	730	180	120	20	22	<10
1,1-Dichloroethene	41	<10	<10	<10	<10	<10
Toluene	13	<10	<10	<10	<10	<10
Tetrachloroethene	<10	<10	<10	33	<10	55
Acetone	<10	<10	150	120	<10	<10
Chloromethane	<10	<10	83	92	<10	<10
Bromomethane	<10	<10	36	35	<10	<10
2-Butanone	<10	<10	14	<10	<10	<10
Carbon Disulfide	<10	<10	<10	24	<10	<10
Total VOCs	31,784	1,620	4,903	454	2,262	55

Degradation-Desorption Relationships in the Treatment of Contaminated Soils Using Modified Fenton's Reagent

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Despite over two decades of research and implementation of innovative technologies for the destruction of biorefractory organic hazardous wastes, some contaminants are still not effectively treated, particularly if they are sorbed to soils or if they are transformed into refractory products. For example, 2,4,6-trinitrotoluene (TNT) remains a challenge to both biological and chemical treatment processes, primarily because some of its degradation products polymerize or are degradative end points (Bradley *et al.*, 1994). For most hydrophobic contaminants, desorption often limits the rate of treatment in soils and groundwater. In pump and treat groundwater remediation, hundreds of pore volumes of clean water are often required to achieve acceptable contaminant concentrations. Although soil washing may be effective for enhancing contaminant desorption, the wash water (which usually contains high concentrations of surfactants) must then be treated, often in a separate reactor. Although a recent theme in site remediation has been to deemphasize process engineering in favor of natural attenuation as a solution for the clean up of hazardous wastes, the long-term monitoring required for natural attenuation is not always cost effective; furthermore, responsible parties remain liable until site closure is reached. Therefore, there is an increased interested in systems for the active treatment of hazardous wastes, such as advanced oxidation processes (AOPs), in which soils can be treated rapidly.

The use of modified Fenton's reactions for the treatment of contaminated soils and groundwater has recently seen increased emphasis because of its ability to rapidly oxidize a range of biorefractory contaminants. Such Fenton-like reactions are based on the catalyzed decomposition of hydrogen peroxide (H_2O_2) by iron (II) to form hydroxyl radicals (OH•):

$$H_2O_2 + Fe^{2+} \varnothing\ OH\bullet + OH^- + Fe^{3+} \qquad (1)$$
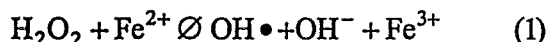
Hydroxyl radical, a non-specific oxidant that reacts with most organic compounds at near-diffusion controlled rates (i.e., $> 10^9\ M^{-1}\ sec^{-1}$) (Haag and Yao, 1992), readily attacks even highly chlorinated aromatic and olefinic compounds. Therefore, Fenton-like reactions have the potential to oxidize a large number of hazardous organic compounds when they are present in aqueous solutions.
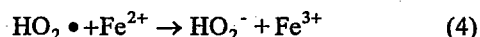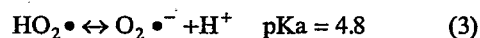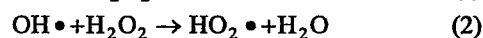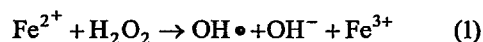
The majority of environmental contaminants are hydrophobic and are therefore sorbed to soils and subsurface sediments. Because most contaminants are unavailable for transformation processes in the sorbed state, desorption often controls the rate at which they are treated by ex situ and *in situ* processes. For example, Sedlak and Andren (1994) found that desorption rates of sorbed PCBs were not enhanced by Fenton-like reactions and that the PCBs were not available for oxidative attack by hydroxyl radicals. However, the enhanced degradation of sorbed contaminants has been documented using more vigorous Fenton-like reactions (hydrogen peroxide concentrations • 2%) (Watts et al., 1993; Watts et al., 1994; Spencer et al., 1996). For example, Watts et al. (1994) found that at successively high hydrogen peroxide concentrations, sorbed hexachlorobenzene was degraded more rapidly than it was naturally desorbed. Gates and Siegrist (1995) also found enhanced desorption of trichloroethylene at hydrogen peroxide concentrations • 2%. Watts and Stanton (1999) documented that, although hexadecane sorbed to soils showed no measurable gas-purge (GP) desorption over 72 hr, under Fenton-like conditions it was oxidized > 90% within 24 hr (with 82% recovery of ^{14}C-labeled hexadecane as $^{14}C\text{-}CO_2$), confirming that sorptive processes can be overcome by vigorous Fenton-like reactions. Although the overall dynamics of the enhanced degradation of sorbed contaminants are evident from recent studies, the mechanisms occurring in these systems have not previously been elucidated. The contaminants could

be displaced from the soil surface by hydrogen peroxide, hydroxyl radicals, or reductants; alternatively, the contaminants could be oxidized in the sorbed state by a reactant that is generated through vigorous Fenton-like reactions.

The standard Fenton's procedure for generating hydroxyl radicals involves the slow addition of dilute hydrogen peroxide to a degassed solution containing the substrate and excess iron (II). This procedure is well documented and produces nearly quantitative stoichiometric generation of hydroxyl radicals. However, the standard Fenton's process is ineffective in degrading sorbed contaminants (Watts et al., 1993).

Hexachloroethane, which has negligible reactivity with hydroxyl radicals, was transformed more rapidly in modified Fenton's reactions (•2 % hydrogen peroxide) than it was lost by gas-purge desorption, suggesting the existence of a non-hydroxyl radical mechanism. Addition of excess isopropanol to scavenge hydroxyl radicals slowed, but did not stop, the desorption and degradation of hexachloroethane. In the presence of the reductant scavenger chloroform, hexachloroethane did not desorb and was not degraded, suggesting that a reductive pathway in vigorous Fenton-like reactions is responsible for enhanced contaminant desorption. Fenton-like degradation of hexachloroethane yielded the reduced product pentachloroethane, confirming the presence of a reductive mechanism. In the presence of excess isopropanol, toluene, which has negligible reactivity with reductants, was displaced from the soil but not degraded. The results are consistent with enhanced contaminant desorption by reductants, followed by oxidation and reduction in the aqueous phase.

The modified Fenton's reactions that have been most effective in degrading sorbed contaminants and compounds that are not reactive with hydroxyl radicals (e.g., hexachloroethane) use excess hydrogen peroxide, which may promote the following reactions to generate other reactive species, such as, perhydroxyl radical ($HO_2\bullet$), superoxide radical ($O_2\bullet^-$), and hydroperoxide anion (HO_2^-):

$$Fe^{2+} + H_2O_2 \rightarrow OH\bullet + OH^- + Fe^{3+} \qquad (1)$$
$$OH\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2O \qquad (2)$$
$$HO_2\bullet \leftrightarrow O_2\bullet^- + H^+ \quad pKa = 4.8 \qquad (3)$$
$$HO_2\bullet + Fe^{2+} \rightarrow HO_2^- + Fe^{3+} \qquad (4)$$

Hydroperoxide anion has been shown to be an effective reductant of a number of oxidized species (Farhataziz and Ross, 1977). Alternatively, hydroperoxide may be involved in another redox couple to produce hydrated electrons. Our initial results on Fenton-like reductions show that a compound's reactivity with hydrated electrons correlates well with Fenton-like reductions.

The use of vigorous Fenton-like reactions to treat sorbed contaminants in soils and groundwater has a number of advantages over other soil and groundwater treatment processes, including 1) a combined enhanced desorption-degradation process that can be conducted in situ or ex situ, and 2) coexisting oxidative and reductive mechanisms that may provide the potential to treat a wider range of contaminants than can be treated by OH• mechanisms alone. The potential for generating both oxidants and reductants in modified Fenton's reactions has important implications in waste treatment. A Fenton's system that generates both species has the potential to desorb contaminants, oxidize reduced contaminants (e.g., monocyclic aromatic hydrocarbons, alkenes, PAHs), and reduce oxidized contaminants (e.g., carbon tetrachloride, 1,3,5-trinitrobenzene). Furthermore, many degradation products that are relatively unreactive with OH• may be transformed by reductants in the system, which may enhance the potential for contaminant mineralization by Fenton-like reactions. Therefore, vigorous Fenton-like reactions in which reductants are generated may provide a universal treatment matrix in which contaminants are rapidly desorbed from solids and sludges, followed by transformation through both oxidative and reductive mechanisms.

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Containment Technology and Monitoring

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Subsurface vertical barriers have been used to control ground-water seepage in the construction industry for many years. Recently, much attention has been focused on the use of containment technologies as supplemental and stand-alone remedial options for hazardous waste sites to prevent or reduce the impact of contaminant sources on ground-water resources. Containment systems can be classified as active (e.g., ground-water extraction to control hydraulic gradient) or passive (e.g., physical barriers only). Frequently, containment systems employ a combination of active and passive components, depending on the remedial objectives and complexity of the hydrogeologic setting. Such systems commonly incorporate low permeability vertical barriers (walls) keyed into an underlying aquitard (floor), a low permeability cover (cap) to prevent the infiltration of precipitation, extraction and/or injection wells, trenches, and a network of monitoring wells.

Soil-bentonite (slurry) cutoff walls are the most common types of vertical barriers used at hazardous waste sites. Potential failure mechanisms of vertical barriers can be classified as design errors, construction defects, and post-construction property changes. Proper design will reduce the potential for errors associated with wall configuration, materials incompatibility and other factors. Construction defects may form high hydraulic conductivity "windows" in an otherwise low hydraulic conductivity barrier. Post-construction property changes may result from wet-dry cycles due to water table fluctuations, freeze-thaw degradation or chemical incompatibility between the barrier components and NAPLs.

The performance of hazardous waste containment systems has generally been evaluated on the basis of construction specifications. Specifically, most systems are required to maintain hydraulic conductivity of a vertical barrier below a specified value, typically less than 1×10^{-9} meters per second (m/s). During construction, the use of appropriate field quality assurance (QA) and quality control (QC) testing is essential to ensure that the design performance specifications are satisfied. Despite rigorous field QA/QC, the unintentional formation of preferential pathways within a vertical barrier is still possible. Whereas the success of a construction dewatering vertical barrier system may be judged by the ability of the barrier to limit ground-water leakage to quantities that can reasonably be extracted, there are no uniform methods to reliably measure and document the hydrologic performance of existing and proposed hazardous waste containment systems.

To determine whether a containment system is protective of human health and the environment, leakage from the system into the environment must be evaluated. Several geophysical techniques have been identified as potentially applicable for the indirect detection of defects associated with vertical barriers. These techniques include ground penetrating radar, electrical resistivity and continuous-wave microwave technologies. Unfortunately, the resolution necessary to identify small scale, yet potentially significant breaches in a containment system may be beyond the ability of much of the instrumentation currently available. Additionally, the high costs of data acquisition and difficulties associated with data interpretation are some of the problems that plague many of the geophysical techniques.

Hydrogeological techniques may be used to determine whether leakage is occurring, and if so, estimate the rate of loss from the system. If it is determined that a significant volume of groundwater is exiting the system, then the location and magnitude of the leak(s) must be established to ascertain whether major repair efforts are necessary to maintain a protective remedy. The hydraulic signature associated with a containment system leak is dependent on the magnitude of the difference in hydraulic head across the barrier wall, the extent of the leakage, and the hydraulic conductivities of the vertical barrier, window and surrounding aquifer materials. Although spatial variations in water levels have been used to identify gross construction defects in ground-water containment systems, no specific protocols/methodologies have been developed to evaluate whether or not ground-water containment systems are operating as designed.

By analyzing the relationship of the hydraulic head distribution inside and outside the containment system, it is possible to assess whether or not the system is operating as designed and which potential transport mechanisms are most significant and require further evaluation. Under ideal conditions, the hydraulic head will be lower inside a containment system relative to that outside the system. Relatively small differences in hydraulic heads inside and outside a containment system indicate the lack of significant active hydraulic forces for advective transport of contaminants. However, due to the concentration gradient across the barrier, diffusive flux from the system is still possible.

While the hydraulic heads inside and outside a containment system have been used to identify gross system failures, little attention has been given to monitoring the changes in hydraulic heads with time. Temporal water level fluctuations should be evaluated in conjunction with spatial head variations to assess whether or not containment is effective.

It may be possible to identify the general location of suspected leaks indicated by spatial and temporal water level fluctuations using existing monitoring systems. However, the identification of specific leak locations and discharge rates may require additional three-dimensional hydraulic characterization and the installation of additional piezometer clusters. Analysis of sufficiently detailed piezometric head data may allow the identification of subtle changes in the hydraulic head distribution, thereby indicating the general locations of potential leaks in a vertical barrier. Until recently, such an undertaking would be prohibitively expensive, due to the high cost of installing the large number of monitoring wells necessary to adequately define the hydraulic head distribution around a barrier wall. However, with the development of several relatively inexpensive small diameter piezometer installation technologies, it may be possible to install a sufficiently large number of small diameter monitoring points to identify the hydraulic signatures associated with containment system leaks. Similarly, information obtained from cone penetrometer surveys may be useful to identify similar hydraulic signatures.

Additional research is needed to provide a better understanding of the complex hydraulics associated with leaky containment systems. Such insight could be used to enhance existing performance monitoring systems and aid in the design of new monitoring systems and allow the estimation of monitoring point spacing requirements (vertically and horizontally) necessary to detect containment system breaches. Given the current interest in containment systems, as either supplemental or stand-alone remedial alternatives, and the lack of adequate performance monitoring strategies at most existing hazardous waste sites utilizing containment technologies, there is an immediate need for a general protocol for evaluation of containment systems.

Hydraulic Fracturing Overview and Issues

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In situ remediation of soil or groundwater depends upon accessing the contaminant, either to remove it, to destroy it, or to immobilize it. Hydraulic fracturing provides the unique opportunity to create zones *in situ* that effect or enhance a chosen remedial process. In this sense, it enables remedial processes, but is not a remedial process by itself.

Hydraulic fracturing involves injecting fluid into an open well at a pressure such that a crack, or fracture, forms within the surrounding soil, and continuing injection to dilate the fracture and fill it with beneficial material. Most fractures are created with slurries of granular solids that have desirable chemical or physical properties. The first, and still most widely used application, couples sand-filled fractures to soil vapor extraction (SVE) or pump-and-treat recovery. This technique results in highly permeable layers that increase the flow rate of a well, typically by one to two orders of magnitude. However, environmental applications of hydraulic fracturing have advanced beyond the initial uses since it was first applied twelve years ago in EPA research projects.

Uses of Hydraulic Fractures

Increases in discharge improve the performance of soil vapor extraction, free-product recovery and other fluid-based technologies in tight formations where they might otherwise be infeasible. Typically, results increase discharge by factors ranging from 10 to 100, and increase the distance affected y the well 10 times of more compared to control wells. Multiple fractures can be created to focus subsurface flow into zones that can not be effected by conventional wells.

Alternatively, fractures can be used to admit beneficial fluids. Insufficient oxygen too frequently limits *in situ* bioremediation, and hydraulic fractures can be used to improve air injection during bio-sparging or bio-venting. The flux of injected air around a fracture in low permeabil-

ity soil is particularly widespread and uniform. Additionally, nutrient or oxygen-rich solutions could be injected through fractures to stimulate biological systems. Likewise, heated air or steam can be injected to improve the volatility and mobility of contaminants. Solvents and solvating solutions, which mobilize or coalesce contaminants, can also be injected through fractures.

Sand-filled fractures generally are used in these applications because of the low cost of sand. Other materials may be considered if a secondary remediation technology is to be implemented as a polishing process after primary recovery.

Hydraulic fracturing applications are not restricted to the movement of fluid. Fractures can also be used for the emplacement of granular solids that have the capacity to destroy or immobilize contaminants. Hydraulic fracturing methods have been used to create permeable reactive barriers filled with zero valent iron for the purpose of destroying chlorinated compunds dissolved in groundwater. Other barriers have been created with granules of potassium permanganate, which create highly oxidizing conditions that destroy organic solvents and other compounds. Less potent, oxygen-producing peroxides have been placed with fracturing techniques to stimulate aerobic degradation. Other examples of beneficial materials that can be injected as fracturing slurries include activated carbon or other materials for adsorption of contaminants, inoculated porous solids to initiate bioremediation, and electrically conductive materials as electrodes.

Variations in techniques and the spectrum of materials that can be used permit hydraulic fracturing to target petroleum hydrocarbons such as gasoline, diesel, jet fuel and motor oils, chlorinated solvents such as trichloroethylene (TCE) and perchloroethylene (PCE), and inorganic contaminants such as hexavalent chromium, nitrates, arsenic and selenium and even radionuclides such as uranium and strontium. Fractures can be placed to access

sub-surface source zones (hot-spots) or intercept contaminant plumes in soil for the purpose of destroying or removing the contaminants.

Because hydraulic fracturing is a delivery technique, neither the list of target contaminants nor the repertoire of remedial process can be considered exhaustive, and materials yet to be invented may also be usable. Some of the features and advantages are listed in Table 1.

Hydraulic fracturing is applicable to a wide variety of site conditions and contaminants. It can be applied at depths of 5 to 150 feet or greater in either saturated or unsaturated soils. It has been demonstrated from Maine to California in a variety of soils including low permeability clays deposited as glacial drift, lacustrine or overbank sediments, residuum on limestone, saprolite, in shales and siltstones, and in sand and gravel aquifers. Fractures can be created around and under most structures. The technology appears viable for all but the smallest jobs.

Methods of Creation

The fundamental processes of creating fractures by injecting a fluid is straightforward: the fluid is injected into a borehole until the pressure exceeds some critical value and a fracture nucleates. This method can create a fracture in most naturally occurring materials, from rock to unlithified sediment or soil. Once the fracture nucleates, fluid continues to be injected, propagating it away from the borehole.

The different methods of creating hydraulic fractures share a common feature in preparation and handling of the injected slurry. While fractures can be created with water, most hydraulic fracturing relies upon viscosified water that can more effectively transport solid particles. Guar gum gel is the most typical viscosifier used. Guar gum is a food additive derived from the guar bean and is composed of short-chained polysaccharides. Mixed with water, guar gum forms a fluid of moderate viscosity, similar to mineral oil. Adding a crosslinker causes the polymer chains to link and form a thick gel capable of suspending high concentrations of heavy solid granules. The non-Newtonian character of the gel permits it to be pumped and to flow through fairly small openings. The properties make guar gum gel ideal for filling fractures with solid material. An enzyme added to the gel eventually breaks the polymer chains, allowing recovery or dispersal of the thinned fluid from the fracture. In some cases the reactivity of the solid material to be transported into the fracture precludes the use of guar gum gel. For instance, potassium permanganate granules are best carried as aqueous slurry viscosified by mineral additives.

Hydraulic fracturing with slurries composed of viscosified water and solid granules requires several specialized pieces of equipment. Tanks, hoppers, vats, etc are needed to handle the materials. A mixer is required to blend the water, viscosifiers, and other reagents with the solids. The method also requires a pump capable of handling slurry that contains high concentrations of solid particles, which may be abrasive. In most cases, positive displacement pumps are used.

Variants among hydraulic fracturing methods have been adopted to accomplish various objectives. For instance, fracturing methods used to create vertical permeable reactive barriers in an aquifer differ from those that provide flow enhancement to wells. Generally, the different methods seek to exploit local geophysical conditions to influence the form (orientation, extent, aperture, and direction) of the resultant fracture.

Table 1. Features and Advantages of Hydraulic Fracturing

Product Features	Advantages
It is a delivery system	Can be used to enhance a variety of remediation processes Can place both solids & fluids at desired locations Can be adapted to new remediation processes; and thus will remain viable in many situations
Enhances *in situ* remediation & control	Remediation can be accomplished w/o massive & expensive excavation/removal of soil Limits exposure to workers/others
Requires fewer surface access points or wells than conventional processes	Fewer wells=less cost for installation/O&M Can make a particular remediation economically feasible Less disruption of surface activities
Creates *in situ* remediation zones away from the creation well	Remediation can be established underneath buildings/etc., where surface access is limited
Works in conjunction w/ other remediation processes	Operation/monitoring/verification can follow conventional practice

Wellbore configuration during nucleation influences the initial orientation upon nucleation, so methods intended to create horizontal fractures utilize a short section of open borehole and a mechanical cutter or jet to create a horizontal notch to focus the nucleating stresses in the horizontal plane. Similarly, a long open borehole and vertical notch favor nucleation of a vertical fracture.

Hybrid techniques that combine hydraulic fracturing with high pressure jets are promising methods for creating vertical barriers filled with reactive materials in the saturated zone, particularly at depths where excavation is infeasible. A recent demonstration showed that such hybrid techniques were capable of creating a vertical reactive barrier filled with zero-valent iron at depths below 50 feet.

Some methods attempt to exploit or influence the state of stress in the formation and thereby control the orientation of the fracture. Fracture orientation, after the fracture is nucleated, is strongly controlled by the state of stress in the formation. A fracture tends to form in a plane perpendicular to the direction of the least stress, i.e. the fracture faces find the easiest direction to push the soil apart. If fracturing pressure is exerted simultaneously in parallel features in a formation, such as two adjacent boreholes, the stress field between the features can cause the two fractures to be parallel and to coalesce into a monolithic unit upon intersection. This feature can be useful for creation of continuous barriers.

Methods to control of fracture aperture depend upon the soil. In low permeability media, aperture can be increased by using slurry of greater viscosity or injecting at a greater rate, although substantial increases can not be obtained without increasing the extent of the fracture. In permeable sand and gravels, penetration of the slurry liquid into the surrounding soil can stall the propagation of the fracture, causing subsequent injection to further dilate the fracture.

The process, known as leak-off, requires careful control of slurry rheology.

Design Considerations

Several factors affect the choice of hydraulic fracturing as a remediation tool at the site. Generally the target formations must be below a depth that can be excavated or surface structures and activities preclude excavation. For the installation of permeable barriers, trenching equipment can reach depths of 50 feet or more. If the contamination at the site is confined to the upper few feet, removal will probably be more effective than any *in situ* process, and hydraulic fracturing would not be required.

The presence of surface structures can complicate the placement of fractures. Although fracturing methods can be employed in close quarters, such as inside buildings or crawl spaces, consideration must be given to the interaction between the structures and the fractures. Building foundations or weight may restrict the propagation of the fracture. Light buildings, such as wooden frame constructed on a slab, will effect only the shallowest fractures whereas multistory masonry buildings can deflect fractures that are intended to penetrate underneath the foundation. Sensitive structures, such as rotating process equipment, precision aligned machines, or storage tanks for dangerous chemicals, may not tolerate movement of the ground surface, which is an inevitable result of creating a space in the subsurface.

In order for fracturing to enhance remedial processes that involve fluid delivery or recovery, the fracture must be significantly more permeable than the enveloping formation. Therefore, the relative improvement resulting from hydraulic fractures increases as the permeability of the formation decreases. In most cases, rock or formations of clay and silt are best suited to hydraulic fracturing because they have the lowest permeability.

In Situ Chemical Treatment Using Hydraulic Fracturing To Emplace Fe° Metal and KMnO₄ Reactive Solids

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Introduction

Petrochemicals (e.g., benzene) and organic solvents (e.g., trichloroethene (TCE)) are common and problematic contaminants of concern (COCs) at federal facilities and industrial sites across the U.S. and abroad (Riley et al. 1992; Siegrist and van Ee 1994: API 1995; DOE 1996; USEPA 1997). They are often present in source areas near storage tanks and land treatment sites and in associated soil and groundwater plumes, where they can exist as vapor, dissolved or sorbed phase constituents as well as light- or dense- nonaqueous phase liquids (LNAPLs or DNAPLs). When these COCs are present in low permeability media (LPM) such as silt and clay deposits, there are major challenges with assessment of their behavior and implementation of effective *in situ* remediation technologies (API 1995; DOE 1996). Despite a low bulk permeability ($K_{sat} < 10^{-5}$ cm/s), these COCs contaminate LPM deposits by moving into and through natural pore and fracture networks where they partition into multiple phases (Figure 1). Long-term exposures and unacceptable risk can result from drinking contaminated water, ingesting surface soils, or inhaling vapors that enter basements or that are emitted during showering. In recognition of the need for effective *in situ* remediation methods, DNAPL compounds in LPM deposits was recently ranked as a top environmental restoration need across the DOE Complex (DOE 1996). Similarly, nearly 40% of the underground storage tanks in the world are located on clay soils and *in situ* remediation of LNAPL contamination in these settings has been a major challenge for the petroleum industry (API 1995).

In situ remediation by conventional methods such as soil vapor extraction or biodegradation are often ineffective at LPM sites due to poor accessibility to the contaminants and severe mass transfer limitations (API 1995; DOE 1996; Freeze and McKay 1997). Alternative techniques to enhance *in situ* remediation have been developed utilizing subsurface disruption by soil mixing (e.g., Siegrist et al. 1995, Cline et al. 1997) or the alternative driving forces of electrokinetics (e.g., Probstein and Hicks 1993; Shapiro and Probstein 1993; Ho et al. 1995; Murdoch and Chen 1997). In seeking less intensive methods that could be used over larger areas, multipoint injection and permeation methods have been tested and advanced soil fracturing techniques have been developed (Murdoch et al. 1997a,b; Siegrist et al. 1998a,b, 1999).

This paper presents a synopsis of laboratory and modeling studies and field demonstration and testing activities carried out to evaluate *in situ* chemical treatment using hydraulic fracturing with zero valent iron metal (Fe⁰) or potassium permanganate (KMnO₄) solids to achieve *in situ* destruction of TCE. For a general discussion of advanced fracturing employing reactive media, the reader is referred to Murdoch et al. (1997a,b). A more detailed description of the field demonstration may be found in Siegrist et al. (1999) while details regarding related work with thermally enhanced mass recovery may be found in Siegrist et al. (1998a). Information on supporting laboratory experimentation may be found in Case (1997) and Struse (1999), and in forthcoming papers.
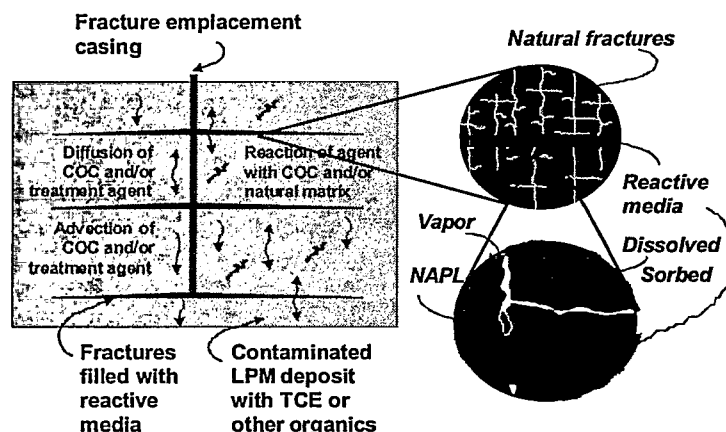
Figure 1. Chemical treatment zones installed using hydraulic fracturing and reactive solids.

Hydraulic Fracturing To Emplace Reactive Solids

### Background on Hydraulic Fracturing and Reactive Media

With soil fracturing, it is feasible to create fractures in LPM deposits by injecting a viscous liquid containing a high content of suspended granular solids (USEPA 1993; Murdoch et al. 1994). The granular solids remain in the fracture after injection and the properties of the solids can be exploited for *in situ* remediation. Hydraulic fracturing normally employs sand as a proppant to fill and support the fracture opening and prevent fracture closure during natural healing processes in unconsolidated deposits. Fractures filled with sand can enhance the rate of recovery of fluids from an LPM deposit or aid the delivery of reactive fluids into it. Alternatively, fractures filled with chemically reactive media such as iron metal or potassium permanganate solids can be used to immobilize or degrade organic contaminants *in situ* (Murdoch et al. 1997a,b; Siegrist et al. 1999).

Zero valent iron metal (Fe°) as a treatment media has been extensively studied during the past five years (Gillham and O'Hannesin 1994; Matheson and Tratnyek 1994; Agrawal and Tratnyek 1996; Muftikian et al. 1996; Liang et al. 1997). Full-scale applications of permeable iron walls for *in situ* treatment of contaminated groundwater are rapidly increasing (Gavaskar et al. 1997; O'Hannesin and Gillham 1998). The reductive dechlorination of TCE to dichloroethene by Fe° is shown in equation 1. The complete dechlorination reaction for TCE to ethene and ethane involves single and multiple electron transfers following pseudo-first order kinetics. Half-lives are reported to be on the order of 30 to 60 min. as normalized for the solution to solid surface area typical of a packed bed of iron particles (Liang et al. 1997; Gavaskar et al. 1997; O'Hannesin and Gillham 1998). The pH of the reacting system tends

to rise, but appears to stabilize in the pH 9 to 10 range due to iron hydroxide precipitation. Key reaction products can include daughter chlorocarbons such as dichloroethenes and vinyl chloride (leading to ethenes and ethanes), hydrogen gas, chlorides, and iron oxide and hydroxide precipitates. Accelerated reaction rates and reduced production of vinyl chloride have been reported with palladized iron metal (Muftikian et al. 1996)

$$2Fe^0 + C_2HCl_3 + 3H_2O \rightarrow C_2H_2Cl_2 + H_2 +$$

$$Cl^- + 3OH^- + Fe^{++} \qquad (1)$$
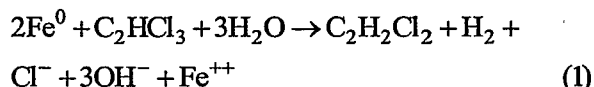
The use of potassium permanganate for oxidative degradation of TCE and other organics at contaminated sites has more recently evolved through initial laboratory experimentation with volatile and semivolatile organics in soil and water (Vella and Veronda 1992; Gates et al. 1995; Yan and Schwartz 1996; Case 1997; Struse 1999). Recently there have been several field applications including subsurface delivery by deep soil mixing or by well injection (e.g., Cline et al. 1997; Schnarr et al. 1998; West et al. 1998). The destruction of TCE by $KMnO_4$ (eqn. 2) can occur by direct electron transfer or free radical advanced oxidation. The rate of TCE degradation is 2nd-order with respect to TCE and permanganate (MnO_4^-) but can be approximated by pseudo-first order kinetics. The reaction is rapid with half-lives on the order of 1 to 2 min or less. The pH of the reacting system can decline to strongly acidic conditions (e.g., pH 2 to 3) depending on the buffering capacity of the reaction system. Key reaction products can include intermediate organic acids along with production of manganese oxide solids (MnO_2)and chlorides. Daughter products such as chlorinated alkanes or chlorinated acids may also conceivably be produced under some conditions but research has yet to fully resolve the occurrence and significance of this.

$$2KMnO_4 + C_2HCl_3 \rightarrow 2CO_2 + 2MnO_2 +$$

$$2KCl + HCl \qquad (2)$$

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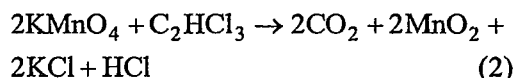
Highlights of Research and Development

During the past three years, the authors have been involved in research and development efforts focused on coupling hydraulic fracturing with chemical treatment methods. The methods and results of this work are described in existing and forthcoming publications (Murdoch et al. 1997a,b; Case 1997; Siegrist et al. 1998a; Struse 1999; Siegrist et al. 1999) and only highlights are provided herein.

Laboratory and Modeling Studies

Laboratory and modeling studies have been focused on permanganate oxidation chemistry and delivery/transport processes since a body of research was already available and/or in progress regarding Fe^0 metal reduction. Laboratory studies have included (1) batch tests to define permanganate oxidation kinetics, (2) development and testing of a permanganate oxidative particle mixture, and (3) intact core studies to quantify permanganate diffusive transport and matrix interactions. Results of this work have revealed that the rate of oxidative destruction of a chlorocarbon such as TCE is 2nd-order with respect to TCE and MnO_4^-. In groundwater at 20C without appreciable natural organic matter, the reaction rate constant is in the range of 0.6 L $mol^{-1}s^{-1}$. Lower temperatures will reduce the rate of organic chemical destruction as will the presence of other oxidant-demanding substances in the system (e.g., natural organic matter). As a proppant for hydraulic fracturing, a permanganate oxidative particle mixture (OPM) was developed that was a pumpable solid comprised of ~50 wt.% potassium permanganate in a mineral gel. The OPM had a chlorocarbon degradation rate that was equal to or greater than that of permanganate alone. This OPM was used in the field trial noted in the following section. Transport studies have also been completed with intact cores of silty clay soil obtained from the field site described below. Diffusive transport of potassium permanganate from a 5 g-$KMnO_4$/L source zone through the silty clay soil was studied to determine oxidation-induced changes in tortuosity due to matrix and contaminant interactions as well as to evaluate degradation efficiency for residual TCE within the media. Studies were made over periods up to 2 months or more with uncontaminated cores, cores contaminated with pure phase TCE, and with glass beads. In uncontaminated cores, diffusing permanganate did oxidize some but not all of the natural organic matter in the soil (~10 to 30% destruction) and did yield MnO_2 deposits but they did not alter system tortuosity. In contaminated cores (~100 to 1000 mg/kg), permanganate transport was retarded due to reaction with the TCE. Oxidation of residual TCE in the silty clay soil was almost complete but tortuosity appeared to be increased, possibly due to more focused and intense MnO_4^- oxidation of residual TCE. Modeling work has included development of a spreadsheet-based screening level model that predicts permanganate diffusive transport away from its location of initial introduction into the subsurface. For example, with a concentration of 40 g/L in a fracture upon emplacement, the enveloping reactive zone was predicted to have extended to 60 cm in total width after 6 months of emplacement (Struse 1999). These modeling results compared well with the field observations made during the field trial noted below.

Field Demonstration and Testing

A field trial was recently completed to evaluate *in situ* remediation using hydraulic fracturing to emplace zero valent iron metal and potassium permanganate solids in the subsurface to chemically treat TCE (Siegrist et al. 1999) (Figure 1). At an old land treatment site, two test cells were installed in silty clay soils with hydraulic fractures filled with either iron metal or permanganate solids at 1.8, 2.4, and 3.6-m depths. The saturated zone was encountered at 3.6-m depth below ground surface (bgs). Fracture emplacement was monitored and soil and groundwater conditions were characterized. After 3, 10 and 15 months of emplacement, continuous cores were collected and morphologic and geochemical data were taken across the fracture zones. Controlled degradation tests were completed using site groundwater with TCE concentrations near 53, 144, and 480 mg/L, equivalent to 0.5, 1.2, and 4.1 g TCE per kg media, respectively. The iron-filled fractures formed a discrete reactive seam less than 1 cm thick, wherein the Eh decreased and reductive dechlorination could occur, but effects in the adjacent silty clay soils were negligible (Figure 2). While the emplaced iron exhibited some surface corrosion after extended emplacement in the subsurface, its reactivity was unaffected. Iron from the fractures degraded TCE at efficiencies of as much as 36% after 24 to 48 hr of contact, which is consistent with Fe^0 packed bed degradation half-lives of 1 to 2 hr. The permanganate-filled fractures yielded a diffusereactive zone that expanded over time reaching 40 cm in thickness after 10 months (Figure 3). Throughout this oxidizing zone, the degradation efficiency was >99% after 2 hr of contact for dissolved TCE at 0.5 and 1.2 mg TCE per g of media. When exposed to higher TCE loadings (i.e., 4.1 mg per g), degradation efficiencies after 10 months dropped to 70% as the TCE load exceeded the oxidant capacity remaining. These efficiencies and rates are consistent with oxidation stoichiometry and previously determined half-lives of <2 min. for permanganate oxidation of TCE. In both test cells there were no marked effects on the chemistry or contamination levels in the groundwater beneath the cells.

Discussion and Conclusions

Discussion

The feasibility of *in situ* remediation of TCE and other DNAPL compounds at LPM sites using reactive solids emplaced by hydraulic fracturing requires consideration of the horizontal continuity, degradation capacity, and longevity of the treatment agents. The results obtained from the work to date enable an interesting contrast between reactive fractures created with surface reactive media (i.e., Fe^0 particles in a guar gum gel) and those created with reactive media that dissolves and permeates into the surrounding soil to produce a wide reactive zone (i.e., $KMnO_4$
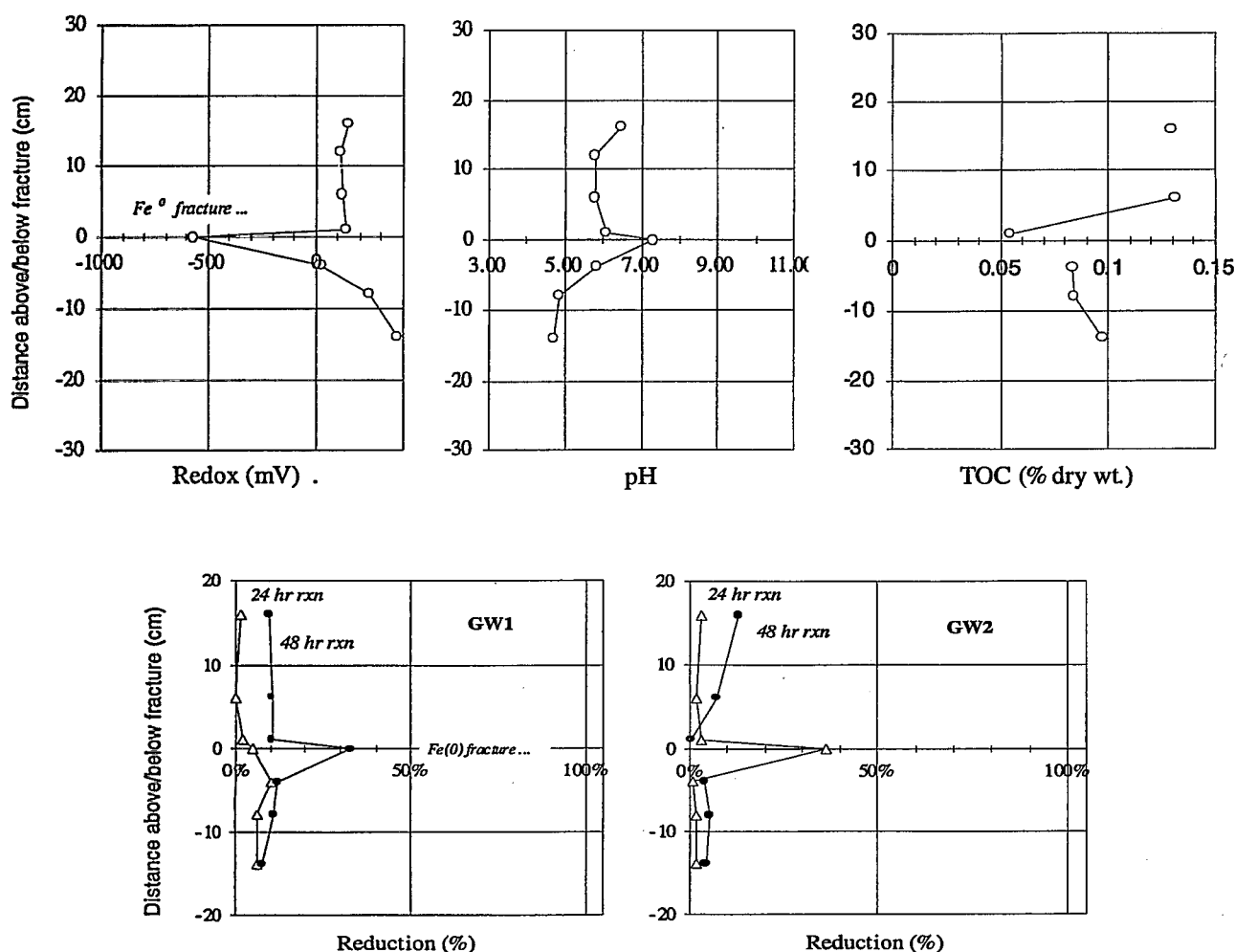
Figure 2. Geochemical properties and TCE degradation potential of Fe^0 metal fracture zones 10 mon. after emplacement in a silty clay deposit (Siegrist et al. 1999). Notes: TCE degradation measured using 5 g of media in 40 mL of GW1 (initial TCE = 477.0 mg/L) or GW2 (initial TCE = 53.7 mg/L)

particles in a mineral gel). During the field trial described, both types of reactive media were handled and emplaced by conventional hydraulic fracturing equipment and methods. Handling of the permanganate was more problematic in some respects but modifications to fracturing equipment or development of encapsulation methods should resolve this issue. In general, the geometry of the reactive media fractures was similar to that of conventional sand-filled fractures emplaced at the same site. Thus, there was no unusual behavior associated with the different fracturing fluids (i.e., iron particles in guar gum gel; permanganate particles in mineral-based gel; sand in guar gum gel).

Hydraulic fractures may bifurcate to form offset segments, which could produce local areas that are avoided by injected material (Murdoch 1995). This challenges the fracture emplacement to be continuous and uniform horizontally with limited breaches through it, a requirement that may require overlapping fractures created at several depths. The Fe^0-filled fractures are discrete layers and appear to have limited effect on the soil deposit beyond the fracture boundaries. Thus any *in situ* degradation of TCE or related compounds must rely on contaminants being mobilized to a fracture and then reacting with the Fe^0 within the fracture. The degradation rates observed in this study were consistent with previous studies suggesting a half-life on the order of 1 to 2 hr for TCE degradation in Fe^0-filled fractures. While slow, this is still rapid enough for high treatment efficiencies to be achieved during a day or less of contact that is achievable for most LPM deposits. For example, if groundwater percolation through the fracture is controlled by the surrounding LPM which has a K_{sat} of 10^{-6} cm/s and a hydraulic gradient of unity, then the retention time in an Fe^0-filled fracture of 5 mm thickness would be on the order of 1 to 5 days depending on the effective porosity. As a treatment zone that relies domi-
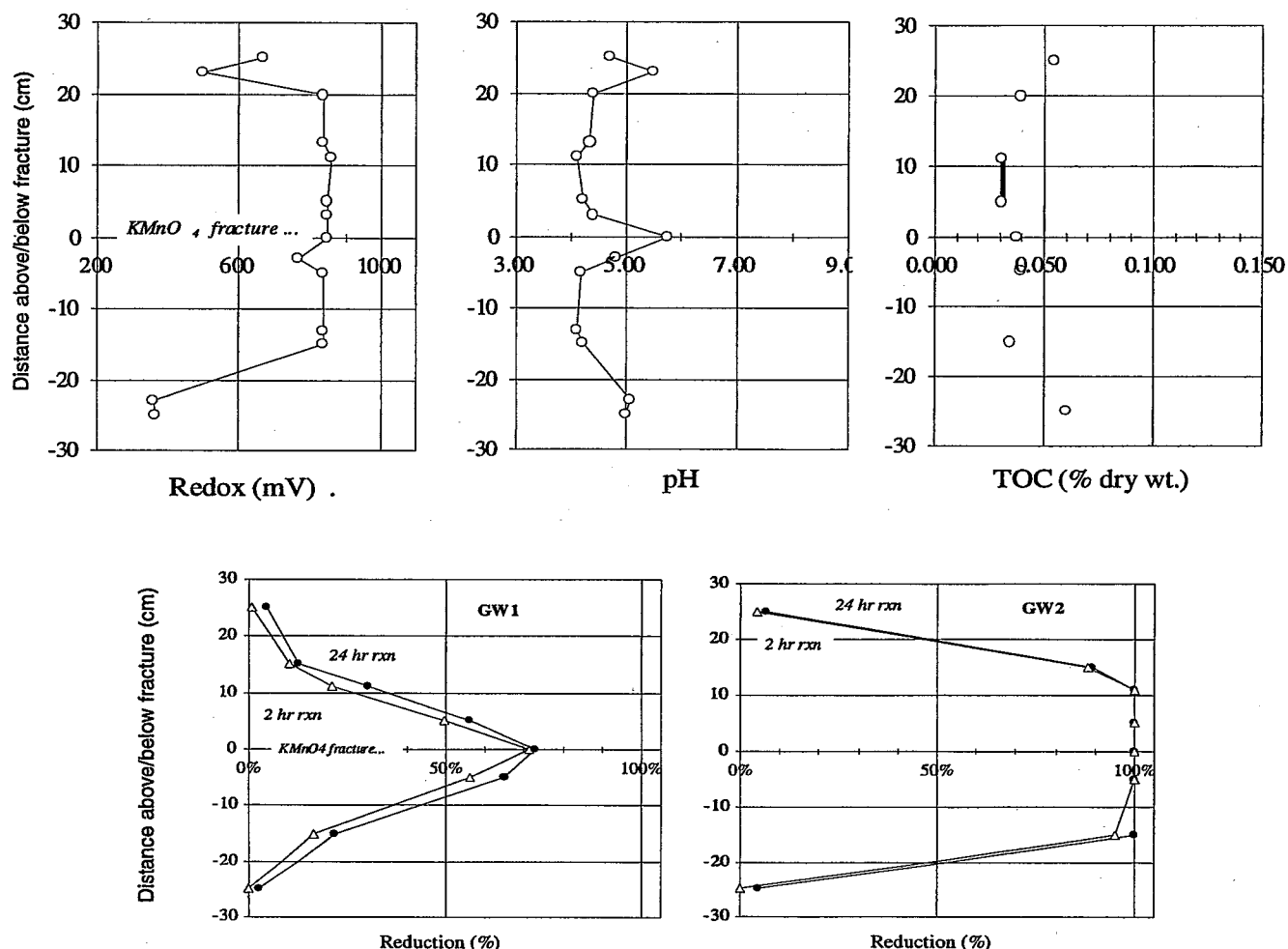
Figure 3. Geochemical properties and TCE degradation potential of permanganate fracture zones 10 mon. after emplacement in a silty clay deposit (Siegrist et al. 1999). Notes: TCE degradation measured using 5 g of media in 40 mL of GW1 (initial TCE = 490.5 mg/L) or GW2 (initial TCE = 50.5 mg/L).

nantly on diffusive transport of contaminants to the iron, the reactivity of the Fe° surface would need to exist for an extended period (e.g., years). Field investigations of iron-filled zones placed in groundwater as permeable treatment walls have revealed reactivity for up to five years (O'Hannesin and Gillham 1998). However, such information is lacking for iron metal emplaced in fractures in a vadose zone without high advection through or across the iron surface. Analysis of the micromorphology of iron particles retrieved from the fractures made in this study revealed some corrosion of the iron surface after residing in the subsurface for nearly 11 months. The effect was limited to a fraction of the available iron surface, however, and it had no apparent effect on TCE degradation (Siegrist et al. 1999).

Fractures filled with a KMnO$_4$ OPM yield MnO$_4^-$ ions that migrate away from their original location, dominantly by diffusion in an LPM deposit but possibly aided by advection driven

by capillary gradients as well. This behavior will produce a zone at least several dm wide where resident TCE will be rapidly degraded, and it could also provide a barrier that would degrade mobile TCE as well. As a result, the gaps between offset fracture lobes or discontinuities between neighboring fractures might be "healed" by the migration of permanganate ions. The field results suggest that TCE degradation is fast and extensive, which is consistent with companion laboratory studies carried out with KMnO$_4$ crystals and OPM. These lab studies revealed nearly 100% destruction of TCE following pseudo first order kinetics with degradation half-lives of <2.4 min. for TCE concentrations up to 800 mg/L (Case 1997). The permanganate degradation of TCE appears to proceed stoichiometrically according to eqn. 2, which can be used to roughly estimate the active life of a permanganate-filled fracture. A 5-mm thick permanganate-filled fracture contains

about 0.4 g $KMnO_4$ per cm^2 of fracture horizontal area. Based on complete oxidation and a stoichiometric TCE demand of 2.5 wt./wt., each cm^2 of fracture can treat about 0.16 g of TCE. This oxidant loading is sufficient to degrade an initial TCE concentration of 1000 mg/kg within a zone of LPM that is 90 cm thick. Alternatively it is sufficient to treat 16 L of percolate with a concentration of 10 mg/L of TCE which is equivalent to a 50-yr life at a deep percolation flux of 1 cm/d. Realistically though, it is anticipated that the oxidant demand of natural organic matter or the advective loss of oxidant out of the treatment region could markedly diminish this life. Based on direct observation in this study, the oxidation capacity within and around the permanganate fractures was striking even 15 months after emplacement.

The cost of remediation using hydraulic fracturing to create chemical treatment zones was roughly compared to that of soil vapor extraction (SVE) enhanced by sand-filled fractures. In general, the reactive chemicals are more expensive than sand and material handling costs are somewhat higher, so the reactive media filled fractures are more expensive to create. The costs for media per fracture amounts to roughly $1000 for iron and $1500 for permanganate as compared to $100 for sand. However, during passive operation, the treatment zones require less resource consumption (e.g., power), less sampling and analysis (e.g., no off-gas), and reduced manpower compared to many SVE systems. As a result, the total estimated costs of the horizontal treatment zone systems are similar to the costs for SVE systems. For a 2.2-hectare site contaminated to 5-m depth, the costs for implementing horizontal treatment zones were estimated to be in the range of $25 to $35/$m^3$ for iron and permanganate zones, respectively. This cost was based on 6-m diameter fractured zones with 1-m overlap and fractures installed at depths of 1.7 and 3.5 m. Assuming no bulk media discounts this yields an estimated materials cost of $2,700K for the iron metal and $3,800K for the permanganate. The installation time was estimated at 140 days for a 3-person crew and equipment, yielding a labor cost including travel and per diem of $450K, plus a mobilization/demobilization cost of $50K.

Conclusions

The work to date has explored two types of chemical treatment zones for in situ remediation at LPM sites contaminated by TCE. Laboratory and modeling studies have been completed and a field trial has been conducted. In the field trial, hydraulic fracturing equipment and methods were used to create reactive zones of Fe^0 metal or $KMnO_4$ OPM in horizontally oriented layers within silty clay soils at depths up to 5 m. The Fe^0-filled fractures produced a reactive seam with limited effect on the surrounding LPM while the $KMnO_4$-filled fractures yielded a broad zone of reactivity within the LPM. With both types of fracture zones, degradation potential for high levels of TCE was sustained even after 10 months of emplacement in the subsurface. Both types of horizontal treatment zones may reduce risks associated with exposure to TCE from a contaminated site. Although the system using iron-filled fractures may leave immobile contaminants in the ground untreated, data from this study suggest that it is capable of degrading mobile TCE and thus may reduce risk by effectively eliminating TCE release from a low permeability unit to the atmosphere or an underlying aquifer. The system using permanganate-filled fractures where MnO_4^- ions are diffusively distributed through a broad region, offers the possibility to both curtail TCE release to the atmosphere or an underlying aquifer as well as destroy TCE throughout a low permeability formation. However, diffusive transport is slow and the rate and extent are highly dependent on the physical and chemical properties of the formation. This approach to remediating low permeability formations using fracture emplaced reactive solids is extremely encouraging. While TCE has been the target contaminant in for studies to date, other organic compounds and also redox sensitive metals might be amenable to such an in situ remediation strategy. While the results to date are promising, this in situ remediation approach is still early in its development and further work is necessary and appropriate to provide needed design, implementation, and performance data for a range of site and contamination conditions.

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In Situ Treatment of Chromium Source Area Using Redox Manipulation

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Introduction

A chrome plating facility was operated at the U.S. Coast Guard (USCG) Support Center, near Elizabeth City, North Carolina, for thirty years. Activities in this shop resulted in the release of chromic acid into the soils below the shop. A detailed characterization of the underlying soils and ground water of the chrome plating shop was performed to provide information on the extent of contamination at the site and the potential for off-site migration and environmental impact.

The National Risk Management Research Laboratory (NRMRL) scientists, in cooperation with USCG personnel have completed a project entitled "Use of Permeable Reactive In-Situ Barrier Wall to Remediate Chromium Contaminated Ground Water" at the USCG Support Center, Elizabeth City, North Carolina. This in-situ permeable reactive barrier wall technique is a very effective method for reducing and immobilizing contaminants like Cr(VI) and TCE present in the ground water, but it has limited effectiveness to reduce contaminants present as sorbed phases in the vadose zone. Most of the Cr(VI) at the USCG Support Center site is present in the vadose zone of the aquifer under an oxidizing environment. While some Cr(VI) was reduced to Cr(III) in the vadose zone sediments, the reducing capacity of these sediments was eventually overwhelmed, and resulted in continuous ground water contamination.

Abiotic reduction by manipulating the oxidation-reduction (redox) status of a vadose zone is a possible approach for in-situ remediation of a redox-sensitive contaminant like Cr(VI). The reduction of the mobile and toxic Cr(VI) to less toxic and insoluble Cr(III) precipitates has been demonstrated to occur in the aqueous system (Palmer and Puls, 1994 and Amonette et al., 1994). Researchers have identified few inorganic reductants and anthropogenic sources of electron donors that can transform the toxic Cr(VI) form to the less toxic Cr(III). Under alkaline to slightly acidic conditions, this Cr(III) precipitates as a fairly insoluble hydroxide, thereby immobilizing it within the soil. Such "natural attenuation" of Cr(VI) is of great interest because it suggests that strict water quality standards do not have to be attained everywhere within a site. Where "natural attenuation" is insufficient to prevent environmental degradation, it may be possible to rejuvenate the "natural attenuation" capacity of the vadose zone by incorporating reductant into the vadose zone. Therefore, the objectives of this study were to evaluate potential reductants and their effectiveness in reducing Cr(VI) present in the soils, the effects of reductants on the geochemical environment, and the interaction between reductants and selected RCRA metals present in the vadose materials.

Methods and Materials

The field site and the hydrogeology of the site have been described in detail elsewhere (Puls et al., 1994). Soil cores were collected from the old plating shop of the USCG Support Center, Elizabeth City, North Carolina. Samples were air dried and passed through a 2mm screen. The <2mm sediment fraction was used in the batch experiments. The amount of Cr(VI) in the soil samples was determined using the phosphate extraction procedure developed by Bartlet and James (1988). Three soil samples from three different cores (6-4, 7-4, and 15-4) and three reductants (sodium dithionite, l-ascorbic acid, and hydroxylamine) were used in this study. A bicarbonate buffer solution (0.1M $KHCO_3$) was used with sodium dithionite and l-ascorbic acid in order to maintain near neutral pH for the reductant solutions. The procedure used was:

- Weigh replicate 5.0 grams air-dry soil into 50 ml polycarbonate centrifuge tubes.

- Add 25 ml 0.05M reductant to the 50 ml centrifuge tube and shake vigorously.

- Immediately measure Eh and pH. Place tubes on a Thermolyne Maxi-Mix III rotating shaker @ 100 rpm for 24 hrs.

- Measure Eh and pH.

- Centrifuge @ 3600X g for 60 minutes.

- Filter supernatant through 0.2 µm Nuclepore membrane filter.

- Analyze Cr(VI) using the Hach method 8023 and Hach ® DR/2010 spectrophotometer, and trace metals with the Inductively Coupled Plasma Spectrometry(ICP).

Phosphate extractions were conducted on the residual sediments following the modified method of Bartlet and James (1988) in order to determine if any Cr(VI) remained on the sediments. These samples were analyzed for Cr(VI) in the same procedure described above.

Results and Discussion

Each reductant used in this study was effective in reducing Cr(VI) in the soils (Figure 1). In this figure, pre-treatment Cr(VI) represents the Cr(VI) concentration extracted with phosphate solution before the reductant was applied. Post-treatment Cr(VI) represents Cr(VI) concentration extracted by phosphate solution determined after the treatment with reductants. Each of the reductants was able to reduce 100% of very high Cr(VI) contaminated samples. Total Cr represented the amount of all chemical forms of Cr present in the extraction after reductant treatment and determined by ICP. The total Cr content in these extracts was negligible except for the l-ascorbic acid. Figure 1b shows that there was 286 to 111 mg/Kg of some form of soluble Cr present in the l-ascorbic acid solution. After 24-hours extraction period, Cr(VI) was not reduced to solid phase of Cr(III) by l-ascorbic acid. O'Brien and Woodbridge (1997) indicated that Cr(VI) may go through step-wise reduction to Cr(V) and Cr(IV) then Cr(III) with the progression of time.

The pH of the reductant solutions without a bicarbonate buffer was less than 4.0 for sodium dithionite and l-ascorbic acid. To maintain neutral pH, the reductants (sodium dithionite and l-ascorbic acid) were made up in 0.1M $KHCO_3$ solution. The $KHCO_3$ buffer was not used with hydroxylamine to maintain neutral pH because hydroxylamine is a weak base. Post treatment pH of all the extractants was very stable after 24 hours shaking with soil samples and remained in the range of near neutral. It was important to maintain neutral pH because adsorption of Cr(VI) on clay particles decreases under neutral or higher pH. Earlier it was mentioned that 100% Cr(VI) has been reduced by these reductants. Therefore, sorbed Cr(VI) must have been released during extraction periods and eventually reduced. After treatment with reductants, the residual sediment samples were used to extract total and insoluble forms of Cr(VI) with hot 0.28M Na_2CO_3-0.5MNaOH solution using a method developed by James et al. (1995). This extraction method has the capability to extract any soluble mineral forms of Cr(VI) in the sediment sample. No extractable Cr(VI) was determined by this method which confirmed that all Cr(VI) in the sediment samples had been reduced by the selected reductants.

The Eh of the solution was monitored after adding reductants at time zero hour (initial Eh) and 24 hours (final Eh). Figure 2 shows that Eh values obtained in the extraction with sodium dithionite were different from the two other reductants. In the sodium dithionite extraction, the initial Eh was more than -400 mV as compared with +80 mV or less for l-ascorbic acid and hydroxylamine. The final Eh in the sodium dithionite extractions was more than -300 mV. The final Eh values did not change under l-ascorbic acid and there were slightly higher Eh values obtained after 24 hours in the hydroxylamine extractions. Therefore, the result shows that sodium dithionite has the highest reduction capacity among these reductants. These reductants not only reduced Cr(VI) but also redox sensitive metals like Fe and Mn. Figure 3 shows that sodium dithionite extractions contained higher amounts of Fe and less Mn as compared with other extractants (l-ascorbic acid and hydroxylamine).

The concentration of RCRA metals (As, Ba, Cu, Cd, Ni, Pb, and Se) in the sodium dithionite extractants were either below the detection limit of the ICP or the NPDWR's MCLG standards for ground water. The result suggests that these reductants did not mobilize these trace elements during the batch experiments.

Conclusions

All reductants reduced Cr(VI) present in the studied vadose materials, and each provided a unique geochemical environment. High concentrations of soluble species of Cr in the l-ascorbic acid extraction suggest that Cr(VI) may have been reduced to lesser oxidation states and remained in the solution. Hydroxylamine reduced a large portion of Mn but negligible amounts of Fe. In contrast, a large amount of Fe has been reduced by sodium dithionite which is effective in reducing Cr(VI). It will be beneficial to have a large reservoir of reduced Fe which will sustain a reactive zone for a period of time and continue to enable the reduction of Cr(VI) present in the vadose zone. Analyses of RCRA metals in the dithionite extractants suggest that there will be no deleterious effect on ground water. Therefore, sodium dithionite has an advantage over other reductants used in this study and it would be the choice reductant for the field project. This research has contributed to the development of a field study, planned for the summer of 1999, to attenuate Cr(VI) present in the vadose zone.

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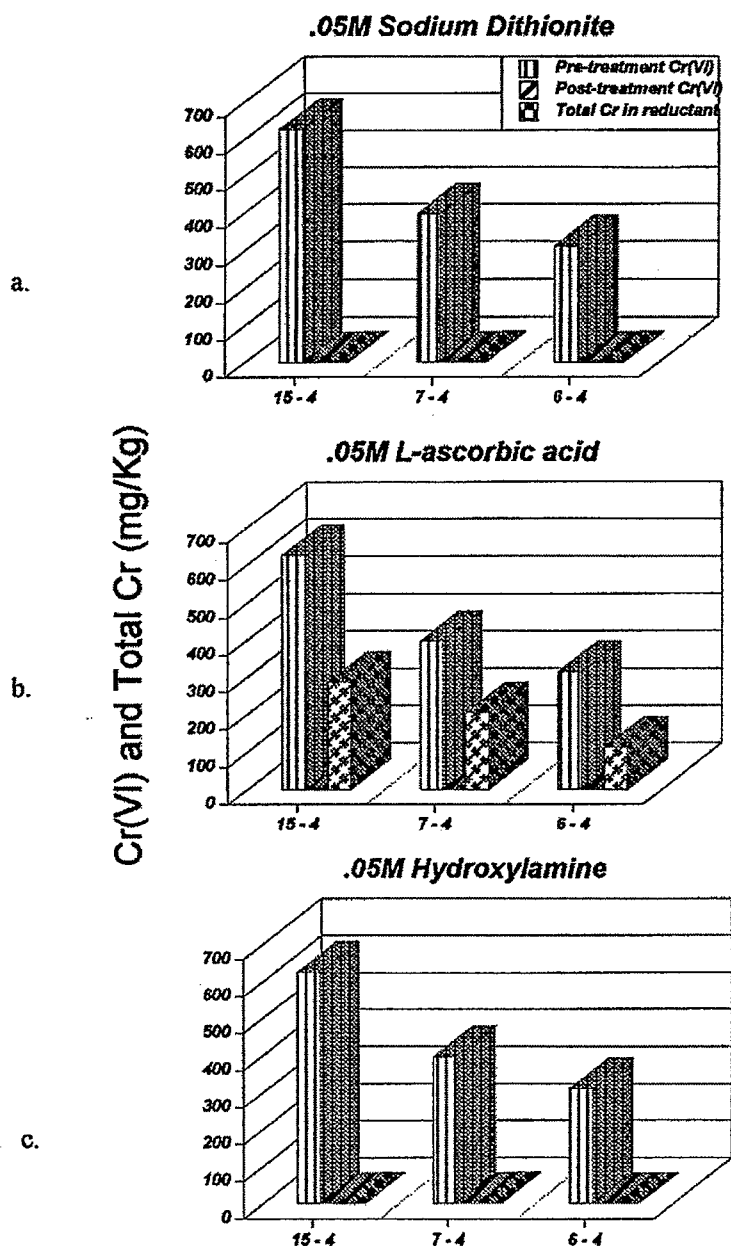This is an extended abstract of the proposed presentation and does not necessarily reflect EPA policy.

Figure 1. Concentrations of initial Cr(VI) compared with post-treatment Cr(VI) and total Cr using three reductants.

In Situ Redox Manipulation for Treatment of Chromate and Trichloroethylene in Groundwater

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As a legacy from weapons production at the U. S. Department of Energy (DOE) Hanford Site in south central Washington State, several chromate groundwater plumes are currently impinging upon the Columbia River. Pump and treat systems are operating at two of the plumes. Because permeable reactive barriers appear to offer several advantages over pump and treat, DOE has decided to test this concept on a third plume. Because these contaminant plumes average about 80 feet below the ground surface, an alternative to "trench and fill" permeable reactive barriers was developed. This alternative, called *In Situ* Redox Manipulation (ISRM), can be installed through conventional groundwater wells.

The goal of the ISRM method is to create a permeable treatment zone in the subsurface to remediate redox-sensitive contaminants. Redox sensitive contaminants in the plume are immobilized or destroyed as they migrate through the manipulated zone. A permeable treatment zone is created by reducing the ferric iron in the aquifer sediments to ferrous iron. The 50-ft treatment zone is created by injecting appropriate reagents and buffers (e.g., sodium dithionite and potassium carbonate) to chemically reduce the structural iron in the sediments. The ISRM approach extends the permeable treatment zone concept to sites where the groundwater contaminant plumes are deep (tens of meters below the ground surface) to be treated by excavation or by trench-emplaced permeable barriers.

For the ISRM process, conventional groundwater wells are placed at the site to be treated. A chemical solution of sodium dithionite is injected into the wells for about 10 to 20 hours. Once the solution reaches the groundwater, it reacts with iron in the soil to form a large barrier. When the groundwater flows through the barrier, the targeted contaminants are destroyed or immobilized. Based on field measurements and calculations, it is anticipated that barriers formed in this manner will remain effective for up to 30 years and require minimal maintenance.

Initial bench-scale batch and column experiments conducted on Hanford sediments evaluated of potential reducing reagents, including dissolved sulfur dioxide, hydroxylamine hydrochloride and sodium dithionite. Once sodium dithionite was selected as a preferred reagent, a variety of batch and column experiments with sediment and dithionite were performed by Amonette et al 1994. These bench-scale studies were used to develop an understanding of the important reactions, final reaction products (i.e., residuals), and nature and fate of any ions released from the sediments and sediment surface coatings under reducing conditions (e.g., mobilization of trace metals).

Dithionite is a sulfur-containing oxyanion which breaks down quickly in aqueous solution to form two sulfoxyl radicals. These radicals react rapidly to reduce ferric iron in minerals and oxides which occur naturally in most aquifer sediments. Amonette et al. (1994) have shown that, within the aquifer, the injected dithionite reacts with structural iron in oxyhydroxide and iron-bearing layer silicate mineral phases, reducing Fe(III) to Fe(II) according to the overall reaction described by equation 1.

$$S_2O_4^{2-}(aq) + 2Fe(III)(s) + 2H_2O \rightarrow$$
$$2SO_3^{2-}(aq) + 2Fe(II)(s) + 4H^+ \qquad (1)$$
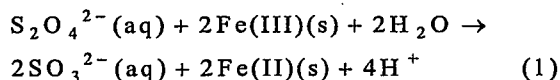
The reduced sediments in the treatment zone can remove redox-sensitive contaminants from groundwater flowing through the zone. For example, the chromate ion ($HCrO_4^-$) is a common groundwater contaminant at many sites, but it is only significantly water-soluble under oxidizing conditions. Within the zone of dithionite-reduced sediments, aqueous chromate reacts with Fe(II) produced by the dithionite reaction (equation 1) and is precipitated as a solid hydroxide (e.g. Cr(OH)3) according to the example reaction described in equation 2:

$$HCrO_4^-(aq) + 3Fe(III)(s) + 4H^+ \rightarrow$$
$$Cr(OH)_3(s) + 3Fe(III) + 2H_2O \qquad (2)$$
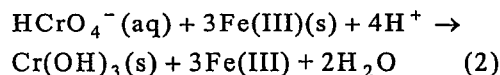
Similar precipitation reactions will occur for other oxidized redox-sensitive metal species.

A proof-of-principle field experiment was conducted in September 1995 at a chromate (hexavalent chromium) contaminated groundwater site at the Hanford Site in Washington State. The proof-of-principle field experiment was a single-well injection test. Its main objective was to determine the feasibility of creating a reduced zone in an aquifer using the ISRM method and to determine the longevity of the reduced zone in a natural environment. The test created a 50-ft (~15-m) diameter cylindrical treatment zone. The three phases of the test consisted of 1) injection of 20,500 gallons (77,000 L) of buffered sodium dithionite solution in 17.5 hours, 2) an 18.5-hour reaction phase, and 3) an 83-hour, 99,600 gallons (375,000 L), withdrawal phase that recovered 87 to 90% of the reaction products. Analysis of post experimental sediment cores indicated that 60 to 100% of the available reactive iron in the treated zone was reduced. Three years later, the treatment zone remains anoxic, and total and hexavalent chromium levels have been reduced from 70 ppb to below the detection limit (<7 ppb). Additionally, no significant permeability changes have been detected during any phase of the experiment. The results are summarized in Fruchter et al, 1996.

During fiscal year 1998, a larger five-well treatability test was installed at the Hanford 100D Area. The test created a permeable reactive barrier 150 feet long and 50 feet in width. The barrier was placed about 500 feet from the Columbia River in a chromate plume with concentrations in the 1,000 to 2,000 ppb range (as chromium). The depth to groundwater was about 85 feet. An average of about 27,000 gallons of buffered sodium dithionite solution was injected in each of the five wells. The sodium dithonite concentration averaged approximately 0.08M. The average reaction phase was 35 hours. Recent monitoring data have shown that chromate concentration in the reduced zone have decreased to below detection limits. In addition, chromate concentrations have also begun decreasing in several down gradient monitoring wells. Monitoring is continuing. In addition to monitoring wells near the site, a series of sampling tubes have been placed along the bank of the Columbia River. Sediment cores will be taken in the reduced zone during the summer of 1999 to determine the amount of ferric iron reduced. The results to date are summarized in Williams et al, 1999.

Based on the success of the treatability test, DOE decided to deploy a full-scale barrier at the 100D site. Current plans call for the expanded barrier to approximately 1,000 feet in length. It will be constructed at the same site as the treatability test barrier. Construction will begin in late fiscal year 1999, and be completed in fiscal year 2000.

Bench-scale tests have shown that dithionite treated soils should also be effective for treatment of dissolved trichloroethylene (TCE) contamination. Based on the bench-scale results, a single well field test was conducted for TCE at Fort Lewis, Washington. Preliminary results indicate that although TCE is being removed, the half-life for the TCE destruction is longer than anticipated from the laboratory data. Additional laboratory tests are being determined to determine the cause, and an additional field test is scheduled for late summer, 1999.

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In Situ Remediation of Chromium Contamination of Soil and Groundwater

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Chromium is a widely distributed element natural to the environment. In its natural trivalent form, chromium has limited solubility. Chromium is also widely used in industrial applications, usually in the soluble hexavalent form. Industrial uses include metal plating, wood treating, and previously in cooling towers. Chromium is one of the most wide-spread metallic contaminants, often dating from industrial applications as far back in time as World War II.

The paper will discuss the geochemical behavior of chromium, as an important basis for the understanding of *in situ* remedial measures to address chromium contamination of soil and groundwater. It then will discuss various remedial alternatives, with a focus on the strengths and weaknesses of each alternative. The alternatives which will be discussed include soil excavation, natural attenuation, ground-water pump and treat systems, zero-valent iron wall reactive barriers, and *in situ* geochemical fixation. Geochemical fixation discussions will include borehole formation of reactive zones, direct-push reductant injection, and a modification of the pump and treat approach. Case histories of the various approaches to *in situ* geochemical fixation are presented, with operational data.

In Situ Reduction of Hexavalent Chromium in Groundwater and Surface Soil Using Acidified Ferrous Sulfate

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Background

The reduction of Cr(VI) by ferrous iron can be described by the overall reaction:

$$Cr(VI) + 3Fe(II) \rightarrow Cr(III) + 3Fe(III)$$
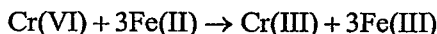
This reaction appears to be appropriate for pH less than 10 and for PO_4 concentrations less than 0.1 mM. Above pH 10, the rate of oxidation of the ferrous iron by dissolved oxygen is greater than the rate of oxidation of ferrous iron by CrO_4. Cr(VI) is a strong oxidant and is reduced in the presence of electron donors such as Fe(II). The Cr (VI) state is generally considered to pose the greatest human health risk because it is more toxic, more mobile, and more soluble than Cr(III). Therefore, the reduction of Cr(VI) to Cr(III) is an important process with regard to aquifer remediation.

The study site consisted of a facility that discharged waste water from spent chromium (Cr) plating solutions to a series of collection ponds. Overtime, Cr, principally in the hexavalent form, leached from the ponds into the shallow groundwater aquifer below (typically 20 - 35 feet below ground surface). As a result, soils in the area have total Cr concentrations ranging from a few ppm to over 30,000 ppm in localized areas of the former wasteponds. Groundwater impacts are highest downgradient from the former ponds and reach levels approaching approximately 4 mg/L (Cr VI). Because the plume is fairly well defined and because the aquifer is composed largely of sand with intermittent lenses of clay and silt, this site represented a potential candidate for an in situ approach to reducing and precipitating hexavalent Cr. Based on these considerations, an approach was developed for performing a field-based in situ Cr reduction study that considered the following elements:

1. Effective chemical reduction and fixation of Cr (VI) can be accomplished using ferrous sulfate, $FeSO_4$. The reaction by which this occurs is:

$$Cr(VI)(aq) + 3Fe(II)(aq) = Cr(III)(aq) + 3Fe(III)(aq)$$
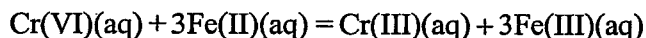
If the pH of the solution is near neutral than the following precipitates can form rapidly:

$$Cr(III) + 3OH = Cr(OH)_3, \text{ and if excess Fe}$$
$$(1-x)Fe(III) + xCr(III) + 3OH = Cr_x Fe_{(1-x)}(OH)_3 (solid)$$

2. The reduction and precipitation of Cr (VI) can theoretically be carried out to treat both groundwater and soil at the site. This is due in large part to the ease with fluids can be introduced and dispersed within the aquifer. Soil treatment should be possible since most hexavalent Cr still remains in the top 2 feet of soil at the site.

Methods

Soil Test Pit Construction and Characterization

Five test pits were constructed at the site. All locations were based on a transect sampling done earlier to determine areas with different amounts of total and hexavalent Cr.

The test pits were used in several ways to determine the effectiveness of in situ Cr reduction for the site. First, two of the test pits were set up as long-term control cells. These cells also had the highest total Cr concentrations of the five, yet were virtually devoid of hexavalent Cr. Thus they presented a unique opportunity to observe changes in speciation patterns over time. These cells have been leached with water (approximately 40 gallons) each month and leachate collected for total and hexavalent Cr determination.

The other test pits served as a "paired test" for observing the effects of ferrous sulfate addition on changes in hexavalent Cr in the soils. One test pit was treated initially

with 8 grams of reducing agent, dissolved in 10 gallons of water and adjusted to pH 4.5. This solution was sprayed on with a hand sprayers. After a 24 hour incubation period, the soil was sampled, extracted with phosphate buffer and Cr (VI) measured. Two days later, the cell was given another treatment of 400 grams of reducing agent dissolved in 10 gallons of water. Again, soil was collected and analyzed after a 24 hour incubation period. Another test pit remained untreated and allowed a comparison of leachate concentrations of Cr (VI) in the treated and untreated cell.

Groundwater Well Installation and Experimental Design:

For treatment of Cr (VI) impacted groundwater, a set of injection and extraction wells were installed. Observation wells were placed between the injection wells and each extraction well at a distance of 2 feet. The observation wells were screened at 25 to 30 feet. Samples were collected at 30 minute intervals after the start of each test and were analyzed for pH, electrical conductivity, dissolved oxygen, hexavalent Cr and chloride. In the first test, 300 gallons of ferrous sulfate solution (200 mg/L buffered at pH 4.5) was delivered to one injection well . At the same time, 300 gallons of tap water with a 50 mg/L spike of chloride (as NaCl) was injected in the other injection well This was also followed with a tap water chaser after all the initial solution had been injected. In this way it was possible to compare the effect of the ferrous sulfate reducing solution to a solution of clean water. The difference (if any) in Cr (VI) concentration after injection and chasing of the two solutions would reflect reduction of hexavalent Cr to Cr (III) by the reducing solution.

A second test was performed about 12 hours after the completion of the first test. In this test, a much higher concentration of reducing solution was injected (almost 2000 mg/L). The purpose of this test was to add excess reducing solution to determine how low hexavalent Cr concentrations could be reduced.

Cr Solubility After Reduction

One of the key factors in assessing whether an *in situ* Cr reduction is a viable remediation alternative will be to establish whether the reduction of Cr(VI) to Cr(III) reduction and subsequent precipitation is stable. Aquifer sand from the area near MW 33 (field moist-saturated) was placed in a plastic acid-washed column fitted with a stop-cock via a small diameter hole to allow water to flow by gravity. Ferrous sulfate reducing solution was added to the column and allowed to mix with the contents over an extended period of time after which the precipitate in the column

was analyzed in a pH solubility test. By comparing the pH vs solubility of Cr in the samples and comparing to known Cr and Fe solids we could determine the solid phase precipitated and then predict the dissolved Cr concentration expected at any pH. By observing solution concentration over time, it would also be possible to determine if any increase in solubility could occur. Solubility results were supported by computer controlled scanning electron microscopy.

Results

Soil Chromium (VI) Reduction

Hexavalent Cr was reduced from approximately 600 mg/kg to about 350 ug/kg in a 24 hour period. When the ferrous sulfate addition was increased to 400 grams per plot, however, almost all the hexavalent Cr in the test pit soil was reduced. Leachate samples from the drain tubes collected about one month after the test pit construction shoed that the treated pits had very low Cr (VI) concentrations on the order of 10 mg/L or less. Leachate from the untreated pit, on the other hand, had hexavalent Cr concentrations on the order of 250 to 300 ug/L.

Groundwater Treatment

The results of the two different groundwater treatment tests shows that where where a 200 ppm ferrous sulfate solution was introduced Cr (VI) decreased from about 3300 ug/L toabout 800 ug/L. Thus ferrous sulfate at 200 ppm will reduce about 60 to 70% of the hexavalent Cr in Unit 1. In the second test, a higher concentration of ferrous sulfate effectively reduced Cr (VI) to below detectable levels. Thus treatment of Cr (VI) in groundwater with a ferrous sulfate reducing solution appears to be a reasonable means of reducing Cr (VI) to levels below detection (<20 ppb).

Results of Stability Experiments

The apparent solubility of Cr in the precipitates is much lower than $Cr(OH)_3$. It appears that a solid solution of $Fe_{1-x}Cr_x(OH)_3$ controls the solubility as predicted from the review of the scientific literature for the conditions of this experiment. The solubility of the precipitated Cr is very low, especially above pH 4.5 where 45 day solubility observations indicated that Cr(III) was only 35 ug/L. At pH 5 the solubility was observed to be only 3 ug/L. Since the aquifer sand and groundwater have a pH near 6 (about 5.7 to 6), it can be assumed that Cr(III) concentrations will remain less than detectable (<1ppb) after treatment with ferrous sulfate. This assumes that the aquifer pH will not decrease substantially below pH 4.5.The Cr precipitate appears to be stable under ambient pH conditions.

In Situ Remediation of Hexavalent Chromium in Groundwater: Practical Implementation

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Overview

Hexavalent chromium [Cr (VI)] presents a problem in our environment due to its high toxicity and carcinogenic effects. In addition, the generally high solubility and mobility of Cr (VI) species tend to increase risk of Cr (VI) transport in groundwater. At a Superfund site (Site) in the Southeastern United States, a conventional pump-and-treat groundwater remediation system is currently serving as an interim action for the hydraulic control and treatment of Cr (VI)-contaminated groundwater. However, an innovative in situ remedy for the full-scale remediation of groundwater has been successfully field-tested at the Site and is now being implemented on a full-scale basis. The in situ remedy, which utilizes an acidic solution of ferrous sulfate, is a subsurface chemical reduction and precipitation technology, whereby sorbed Cr (VI) is displaced from aquifer solids and soluble Cr (VI) is reduced to the trivalent state [Cr (III)]. The residual Cr (III) in groundwater is then immobilized via the formation of an insoluble iron-chromium hydroxide solid solution. Thus, both Cr (VI) and total chromium are effectively treated to below applicable regulatory levels. The acidic ferrous sulfate reagent is injected into the aquifer using chemical metering pumps and vertical injection wells. Data indicate that groundwater concentrations between 0.1 and 4.4 milligrams per liter (mg/l) of total chromium have been effectively treated to below the Safe Drinking Water Act (SDWA) maximum contaminant level (MCL) of 0.1 mg/l.
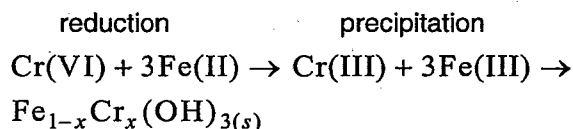
Introduction

The Site is a former saw chain manufacturing facility that operated between 1966 and 1982. Waste rinse waters generated during metal-plating operations and other processes were disposed of by direct discharge to the ground surface in low-lying areas at the Site, referred to as "wastewater ponds". These discharges caused contamination of site groundwater. The main contaminant of concern at the Site is Cr (VI). The plume of Cr (VI)-contaminated groundwater currently has a maximum width of approximately 550 feet and extends approximately 1,750 downgradient from the past source area, and ranges in depth from 20 to 40 feet. Approximately one-half of the groundwater plume is located beyond the property boundary of the Site. The maximum concentration of Cr (VI) within the plume is between 4 and 5 mg/l.

In accordance with the Record of Decision (ROD) for the Site, the groundwater remedy for the Site consists of in situ chemical treatment of the Cr (VI) plume to reduce the mobility and toxicity of the chromium in groundwater. The implementation of the in situ remedy will reduce the overall treatment time needed to achieve remediation of the plume as compared to conventional pump-and-treat technologies. Prior to selecting in situ chemical treatment as the preferred groundwater remedy, site-specific engineering studies, including a demonstration study (pilot-scale test), were conducted at the Site. The site-specific engineering studies concluded that in situ chemical reduction of Cr (VI) to the trivalent state, Cr (III), using ferrous sulfate would be the optimum remedial technology.

By using ferrous sulfate versus other possible reagents, such as ferrous chloride, the ferrous iron provides for reduction of Cr (VI), while the sulfate works to displace sorbed Cr (VI) from aquifer solids. Thus, not only is the groundwater portion of the aquifer effectively remediated, but the solid matrix of the aquifer is also treated. Furthermore, once the Cr (VI) is chemically reduced the residual Cr (III) is then immobilized via the formation of an insoluble iron-chromium hydroxide solid solution. The following equation shows the stoichiometry of the in situ chemical reaction:

$$\underbrace{Cr(VI) + 3Fe(II)}_{\text{reduction}} \rightarrow \underbrace{Cr(III) + 3Fe(III)}_{\text{precipitation}} \rightarrow$$

$$Fe_{1-x}Cr_x(OH)_{3(s)}$$

RD/RA Program

The Remedial Design/Remedial Action (RD/RA) program for the Site has been executed using the observation approach. The observational approach applied to RD recognizes that a complete set of data, which fully characterizes an entire Site, is not feasible, practical, or necessary to obtain. Because of the variability of the aquifer at the Site (e.g., grain size distribution, hydraulic conductivity, stratigraphy, hydraulic gradient, etc.), and the multiple parameters controlling the *in situ* chemical reactions (e.g., pH, oxidation/reduction potential, ionic strength, buffering capacity, etc.), it is not possible to develop a meaningful predictive model except at the "macro" scale. Therefore, the RD for the Site is based on a data set that is only sufficient, and contains multiple contingencies for modifying the design as new data become available.

Under the observational approach, two separate treatment tasks and two full-scale injections related to *in situ* groundwater remediation have been conducted at the Site thus far. The first treatment task consisted of a small-scale injection of ferrous sulfate reagent into a single vertical injection well in the area where the original source of groundwater contamination was located. Because the first treatment task was situated in an area having relatively low Cr (VI) concentrations (0.2 to 0.3 mg/l), a second treatment task, also consisting of a small-scale injection of ferrous sulfate reagent into a single vertical injection well, was conducted in an area of highest groundwater contamination [2 to 4 mg/l of Cr (VI)]. The data obtained from the first two groundwater treatment tasks were used to design the first full-scale injection, which was situated along the upgradient edge of the plume. Data obtained from the first full-scale injection was then used to plan the second full-scale injection, which was situated approximately 200 feet downgradient of the first injection.

Results of Small-Scale Treatment Tasks

The first treatment task consisted of one vertical injection well and a network of seven monitoring wells. An acidic ferrous sulfate (FS) solution was introduced into the subsurface via the vertical injection well using the existing sprayfield infrastructure. The migration of the reagent plume, along with its effect on the aquifer, was monitored using four cross-gradient monitoring wells (to a distance of 20 feet) and three downgradient monitoring wells (to a distance of 30 feet). The required mass of FS injected was based on an estimate of the mass of Cr (VI) in groundwater that required treatment in the selected treatment area and a pre-determined stoichiometric excess (to account for Cr (VI) that would be desorbed from the aquifer). A chloride tracer was also used during the test to monitor the progression of the reagent plume. The final reagent mixture (as injected) contained ferrous iron at 240 mg/l and chloride at 115 mg/l with a pH of 2.6. The reagent was injected over a period of 8 hours.

Overall, the first treatment task was successful in reducing total and hexavalent chromium concentrations in groundwater to below the remediation goal (RG) of 0.1 mg/l. The injected reagent dispersed cross-gradient at a distance of at least 5 feet, but less than 10 feet from the injection point. The reagent plume was observed 12 feet downgradient between 14 and 22 hours after injection and continued moving downgradient, reaching the last monitoring point, 30 feet downgradient of the injection point, by Day 22. The presence of the reagent at each downgradient well was evidenced by a decrease in pH, increase in conductivity, and increase in total and ferrous iron [Fe (II)] and sulfate concentrations. In addition, at each downgradient monitoring location, the reduction of Cr (VI) was instantaneous. A temporary increase (4-to 8-fold) in total chromium was also observed indicating desorption of chromium from aquifer solids. As expected, the reduction of soluble Cr (VI) and desorption of Cr (VI) from aquifer solids happens quickly. In addition, Fe (II) concentrations decrease as desorbed Cr (VI) is reduced. As Cr (III) and Fe (III) start to form an insoluble complex, concentrations of total chromium and total iron decrease.

The second treatment task was situated in an area of highest Cr (VI) contamination and consisted of one vertical injection well and a network of six monitoring wells. The acidic FS solution was again introduced into the subsurface via the vertical injection well using the existing sprayfield infrastructure. The migration of the reagent plume, along with its effect on the aquifer, was monitored using four downgradient monitoring wells (to a distance of 70 feet). The last monitoring point was an extraction well that is part of the current pump-and-treat system at the Site. Deep monitoring wells were installed at 20 and 40 feet downgradient of the injection point to monitor vertical dispersion of the reagent plume. The required mass of FS injected was again based on an estimate of the mass of Cr (VI) in groundwater that required treatment in the selected treatment area and a pre-determined stoichiometric excess (to account for Cr (VI) that would be desorbed from the aquifer). The reagent mixture was again injected over an 8-hour period using the same chemical parameters used during the first injection.

Overall, only limited data were obtained during the second treatment task, as compared to the first task, due to an unexpected flow path observed in the vicinity of the extraction well. The reagent plume did not follow the expected linear path to the extraction well, but rather followed an arched path around the downgradient monitoring wells. The unexpected flow path has been attributed to small-scale spatial heterogeneity within the aquifer. As a result, the data collected during the second treatment task (from temporary direct-push monitoring points installed after injection) represented only post-treatment conditions. However, the data that was collected provided pertinent information, including confirmation that Cr (VI) was again successfully treated to below the RG. Results also indicated that approximately 10 feet of vertical dispersion was achieved.

Practical Implementation of the Full-Scale Remedy

Based on data generated during the two small-scale treatment tasks and an engineering evaluation that identified the most effective and feasible method of injection, the initial phase of full-scale treatment of groundwater was designed and constructed. Full-scale implementation of the groundwater remedy will consist of several lines of vertical injection wells situated approximately 200 feet apart, proceeding in the downgradient direction, with the first injection line located at the upgradient edge of the contaminant plume.

Data from the small-scale tasks indicated that, at a minimum, a 20-foot spacing for injection wells would effectively provide for lateral dispersion of the reagent. However, to provide the most feasible alternative for injection, a 40-foot spacing of vertical injection wells was preferred. Therefore, the first line of injection wells consisted of 11 injection wells, spaced 20 feet apart, which provided a total treatment width of 240 feet. However, to evaluate the effectiveness of lateral dispersion using a 40-foot spacing, FS solution was initially only injected into every other injection well.

The migration of the reagent plume, along with its effect on the aquifer, was monitored using 13 monitoring wells, located 25, 43, 50, 75, 100, 150, and 200 feet downgradient of the injection line. Eight of the 13 wells were situated so that lateral dispersion of the reagent could be evaluated. Three of the 13 wells were installed below and outside the contaminant plume to determine whether the injection causes a displacement of the plume into "clean" areas. The required mass of FS injected was again based on an estimate of the mass of Cr (VI) in groundwater that required treatment in the selected treatment area and a predetermined stoichiometric excess (to account for Cr (VI) that would be desorbed from the aquifer). The reagent mixture was injected over a 96-hour period using the same chemical parameters used during the first injection.

After the first six weeks of post-injection monitoring, data suggested that injection at 40-foot centers was not effective in dispersing the reagent. This was evidenced by the appearance of reagent at a well located 43 feet directly downgradient of an injection point, but the absence of reagent at dispersion wells (that straddle two injection points), located 25 and 43 feet downgradient of the injection line. Therefore, injection into the remaining wells was initiated to provide data to complete an evaluation of full-scale treatment effectiveness. However, in the same week that the second injection was initiated, a trend of increasing sulfate concentrations in the first four dispersion wells was confirmed. The increasing sulfate concentrations in dispersion wells indicated that the reagent plume, although exhausted (i.e., lacking ferrous iron), had successfully reached the dispersion wells. Thus, the 40-foot spacing of injection wells appeared to be effective in laterally dispersing the reagent into the aquifer.

Although the injection along Line 1 was successful in laterally dispersing the reagent, effective treatment over the entire width of the treatment cell was not accomplished due to the exhaustion of the reagent. The exhaustion appears to be due to the buffering capacity of the aquifer in the vicinity of the injection wells. Data for the monitoring well located 43 feet directly downgradient of an injection well support this conclusion. Although treatment was observed at this well (as evidenced by a decrease in Cr (VI) concentration), the pH of groundwater did not decrease, ferrous iron was not detected, and total chromium concentrations did not increase before they decreased (which is an indicator of Cr (VI) desorption from aquifer solids). It appears that the pH of the reagent was buffered, thus causing the pH to increase from 3.0 (pH of the injected solution) to ambient levels, prior to the reagent reaching the well. The increase in pH subsequently caused the oxidation of the ferrous iron to ferric iron. The oxidation of the ferrous iron to ferric iron was complete by the time the reagent arrived at the well. This observation showed that the reducing power of the reagent was exhausted.

A second injection into Line 1 injection wells was then conducted to attempt to overcome the buffering capacity of the aquifer. During the second injection, a larger volume of acidified reagent was injected into the aquifer (over a 30-day period). The pH of the injection solution was also lowered from approximately 3.0 to 2.5 to help overcome the buffering capacity. In addition, enhancements to the chemical deliver system for the reagent solution were made. Unfortunately, during the second Line 1 injection, the aquifer near and around Line 1 continued to buffer the reagent, causing the iron to precipitate. Furthermore, due to the mass of iron precipitate accumulating in close proximity to the injection wells, backpressure within each well increased significantly. The buffering condition near Line 1 is thought to be caused by the proximity of Line 1 to the existing on-site sprayfield, which is used to discharge groundwater that has been chemically treated to remove chromium and other site contaminants. The water that is discharged via the sprayfield is slightly basic and highly buffered.

Since the buffering condition that was observed at Line 1 is not considered to be a site-wide problem, a decision was made to install the second injection line, Line 2, approximately 200 feet downgradient of Line 1, to obtain the data necessary to finalize the RD for the Site. The location of Line 2 is outside the influence of the existing sprayfield and is near the area where the first small-scale groundwater treatment task was conducted, which provided positive evidence of effective groundwater treatment.

Injection along Line 2 is currently underway at the Site. Line 2 consists of 10 injection wells located on 40-foot centers. Preliminary data were not available at the time of abstract submittal.

Design of Cosolvent Flooding Solutions for NAPL Remediation

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Cosolvent flooding is a method for removing NAPLs from aquifer systems using water miscible solvents. Typical cosolvents are low molecular weight miscible alcohols such as ethanol, methanol, isopropanol, n-propanol, and tert-butanol. These alcohols tend to increase the NAPL solubility and decrease the NAPL-water interfacial tension, thus promoting both enhanced dissolution as well as separate phase mobilization. The relative contribution of the two removal mechanisms is largely controlled by the ternary (alcohol/water/contaminant) phase behavior, and either mechanism can be emphasized. With an enhanced dissolution approach, an alcohol that partitions mainly into the aqueous phase is used, while with a separate phase mobilization approach, an alcohol that partitions mainly into the NAPL phase is used. These approaches have been successfully field tested in EPA-SERDP sponsored experiments at the Hill Air Force Base in Utah and at the Dover Air Force Base in Delaware. An additional field test of enhanced dissolution was performed at a dry cleaner site in Florida.

A special variation of the mobilization approach is currently under consideration for chlorinated solvent (DNAPL) remediation. This new approach uses a low density alcohol which partitions strongly enough into the chlorinated solvent phase that it swells it and turns it into an LNAPL. This technique will be field tested this coming year at the Dover Air Force Base. The different cosolvent flooding approaches may benefit from the addition of another chemical component. This addition could be done for one of four reasons. First, a high molecular weight alcohol, such as pentanol or hexanol typically exhibits a stronger cosolvency effect than the lower molecular weight alcohols.

Although the high molecular weight alcohols are not miscible with water, they can be blended with the lower molecular weight alcohols to form a miscible flooding solution. This approach results in a more effective enhanced dissolution flooding solution.

Secondly, a high molecular weight alcohol, being hydrophobic, tends to preferentially partition into the NAPL phase, swelling it. Thus a mixture of low and high molecular weight alcohols can form a more effective separate phase mobilization flooding solution.

A third reason for adding another component to the flooding solution is to alter its density. It may be difficult to deliver and recover a light alcohol flooding solution in some situations. The addition of a dense salt or sugar can increase the flooding solution density until it is comparable to the resident pore water, and this approach could be used for either enhanced dissolution or for NAPL mobilization.

Finally, the partitioning of some low molecular weight, miscible alcohols can be altered by the addition of a salt. The general tendency is for the addition of the salt to increase the degree of alcohol partitoning into the NAPL phase, and this approach could be used to promote NAPL mobilization with NAPL swelling.

It is expected that different sites will require different approaches, and it is not yet known which formulations will prove to be the most efficient in general situations. The issues of contaminant separation, and cosolvent recycling and reinjection will likely be central to the ultimate choice of cosolvent flooding solution composition for a given site.

In Situ Flushing for Enhanced NAPL Site Remediation: Metrics for Performance Assessment

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Remediation technology performance testing requires a demonstration that acceptable risk reduction has been achieved in a cost-effective manner and gathering sufficient evidence to establish that the observed risk reduction resulted from the application of the cleanup technology. Here, by risk reduction we mean a decrease in the concentrations or the total mass or mobility or toxicity of the NAPL constituents of concern at the site. We will focus on technical measures of performance, and do not consider other factors (e.g., stakeholder acceptance). The level of site-specific testing required to establish credibility in the innovative remediation technology is a function of the ease of treatment of the contaminant matrix and the hydro-geologic complexity of the site. Greater amount of testing is usually required at sites with highly complex hydro-geology (e.g., heterogeneous aquifers) and recalcitrant contaminants that are difficult to treat

Field-scale tests of in situ flushing techniques involving alcohols or surfactants can be evaluated based on several metrics that measure the technical performance. The strongest proof of technology performance is based on consistency among multiple lines of evidence, all pointing to similar levels of risk reduction. Commonly, the performance metrics are based on a decrease in NAPL constituent concentrations in soils or groundwater, either within the test zone or at some compliance point/plane downgradient from the test zone.

For this purpose, NAPL constituent concentrations in soil or groundwater samples taken before, during and after the in situ flushing test can be compared to estimate the total NAPL mass removed and the spatial distribution of the NAPL mass remaining within in the target zone. Local information from such point measurements is quite variable, and therefore introduces significant uncertainty in performance assessments unless a sufficiently large number of samples are collected. Alternatively, technology performance can be based on spatially integrated information, as might be the case with the use of inter-well partitioning tracers tests and the total NAPL mass recovered at extraction wells during the alcohol or surfactant flood. Information from such integrated metrics is based on much larger support volumes, and as such is usually much less variable. However, averaging over much larger spatial domains can lead to a decrease in the limits of detection. Data we gathered during several field-scale pilot tests of in situ flushing technology will be used to illustrate the performance metrics and their use in technology assessment.

Application of Pervaporation for the Removal of VOCs and Recovery of IPA from Surfactant-based Soil Remediation Fluids

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Overview

Aquifers and soils contaminated with non-aqueous phase liquids (NAPLs), such as chlorinated solvents and gasoline/fuel components, pose a significant human health and environmental risk as well as a significant technical challenge. Recently, the use of surfactant solutions to enhance NALP solubility has received significant attention because of the potential to dramatically reduce remediation times compared to other technologies. Economic analyses of the surfactant enhanced aquifer remediation (SEAR) process have concluded that reuse of the surfactant is necessary to make the process cost effective.

The EPA was involved in a Department of Defense Environmental Security Technology Certification Program project on surfactant-based soil remediation. The objective was to integrate the subsurface SEAR process with above ground surfactant recovery and reuse processes. The surfactants were used to solubilized subsurface contaminants. Once the solution has been pumped out of the extraction wells, the contaminants will be removed by pervaporation. To be able to reconcentrate and reuse the surfactant, micellar enhanced ultrafiltration (MEUF) was used in the field. Here, we will discuss and present the design criterias, operating procedures and results for the pervaporation system of the field demonstration.

The field demonstration took place in spring 1999 at Camp Lejeune, Jacksonville, North Carolina. This Marine Corps Military Base was contaminated mainly with tetrachloroethylene due to a dry cleaning operation. The field demonstration was divided into three separate tasks. The first task was the injection/extraction of the surfactant. The second task was the recovery of the VOC's by using pervaporation. The third task was the reconcentration of surfactant by micellar enhanced ultrafiltration.

The US EPA National Risk Management Research Laboratory(NRMRL) selected pervaporation as the technology to recover the VOC's. NRMRL performed a series of bench and pilot-scale studies using pervaporation to remove VOC's from surfactant solutions. Based on the performance and results obtained, it was concluded that pervaporation could remove volatile NAPLs from surfactant solutions. Another reason for selecting pervaporation, it was found from previous studies foaming does not adversely affect the performance of this technologies in comparison to other technologies. Technologies such as air stripping, steam stripping, and vacuum extraction experience foaming problems when applied to surfactant solutions.

Technology

Pervaporation is a separation process used for the purification or separation of liquid mixtures. This technology can be characterized as a membrane separation process in which a membrane is selected to produce a desired separation. One side of the membrane is exposed to a liquid feed stream and a vacuum is pulled on the other side. The component or components targeted for removal permeate the membrane, and evaporate into the permeate stream. The reduced pressure of the permeate provides the driving force for the separation. The slowly permeating components remain in the liquid residual, and can be considered purified.

Pervaporation can be used in a variety of industry and environmental applications. The selectivity of the membranes dictates the separation, based on the permeability of the component to be removed from the stream. One application where pervaporation can be used is the dehydration of organic streams, through the selection and use of a hydrophilic membrane. Pervaporation technology is attractive for environmental applications. This field demonstration was a perfect case where pervaporation was the technology to be used. Specifically one of our main goals was the separation of organic compounds from surfactant solutions used in soil flushing technologies. The

targeted component to be removed from the surfactant stream containing dry cleaning solvents was primarily tetrachloroethylene (PCE).

Field Site

The field site is an active dry cleaning shop on the grounds of Marine Corps Base Camp Lejeune in Jacksonville, North Carolina. Once the surfactant was injected, the extracted fluid contained mainly PCE, Surfactant (Isalchem 145 4 PO ether sulfate (IC145), isopropyl alcohol(IPA), calcium chloride, and varsol.

Process

The US EPA NRMRL was responsible for the design of the pervaporation part of the field demonstration. The pervaporation system was composed of a novel vibrating membrane device as well as hollow fiber membrane modules. The system was designed for flow rates up to 10 gpm. The surfactant solution was pumped from the wells to a three way valve at the front end of the pervaporation system. This three way-valve allowed the surfactant solution to flow into an oil-water separator. The over flow from the oil-water separator went to a 1,000 gallon fiber-glass tank. The contents in this tank were fed to the pervaporation system. This stream was sent to a vibrating pervaporation system (V-SEP). After this, it went to a series of hollow fiber membrane modules. The treated surfactant solution was sent to the MEUF storage tank, where the surfactant was recovered by MEUF.

The pervaporation system was designed for unattended operation. The system was set up with automatic controls to regulate flow, feed pressure, vacuum pressure and whenever necessary empty the permeate reservoirs. During the entire demonstration the system was able to monitor a variety of process variables and responded with warnings when conditions exceeded acceptable ranges. The field demonstration lasted around 90 days.

A second pervaporation unit was brought to the site to study the performance of pervaporation in the recovery of isopropyl alcohol(IPA). It was determined due to the high concentration of IPA in the extracted stream that it would be beneficial to study the application of pervaporation to recover IPA in a field site demonstration. The permeate from the MEUF system was the feed to this second pervaporation unit. This system was operated in a batch mode for a period of 10 days.

Operating Conditions

The main pervaporation unit was operated at approximately 1gpm and 40 °C. The system was in operation for 80 days. The following conditions were monitored temperatures, feed flowrate, residual pressures, and permeate pressures. Sampling and analysis were performed three times a week. Some of the analysis was performed on site to determine the required dilutions of the samples to be sent and analyzed in our labs in Cincinnati, Ohio. Undiluted samples were taken and sent to the labs in case of any mistakes and/or human error.

The second pervaporation unit was in operation for 10 days. Several operating conditions were tested. Two different flow rates (3&6gpm) and three different temperatures (40, 50 & 60 °C) were tested for a total of 9 runs. Feed and residual samples were taken every hour. The analyses for these samples were performed on site.

In this paper, the results from this demonstration will be presented. An economic analysis for this technology will be shown to prove the cost efficiency of the process. Preliminary results for the demonstration showed the main objective of removing 95% of PCE was met.

Disclaimer

This is an extended abstract of a proposed presentation and does not reflect USEPA policy.

Coupling *In Situ* Flushing with Other Remediation Technologies

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In situ flushing technologies that employ cosolvents and surfactants have been recently tested at a number of sites. The remediation goal has been to remove non-aqueous phase liquid (NAPL) and reduce the long-term threat to groundwater resources. *In situ* flushing techniques might be coupled with other technologies in a "treatment train" approach to extend the remediation goals to meet end-points such as regulatory maximum concentration levels (MCLs). Technologies such as free phase recovery prior to *in situ* flushing and enhanced bioremediation following a flood will be discussed. A recent DNAPL *in situ* flushing project at a dry cleaner site will be used as an example of technology coupling.

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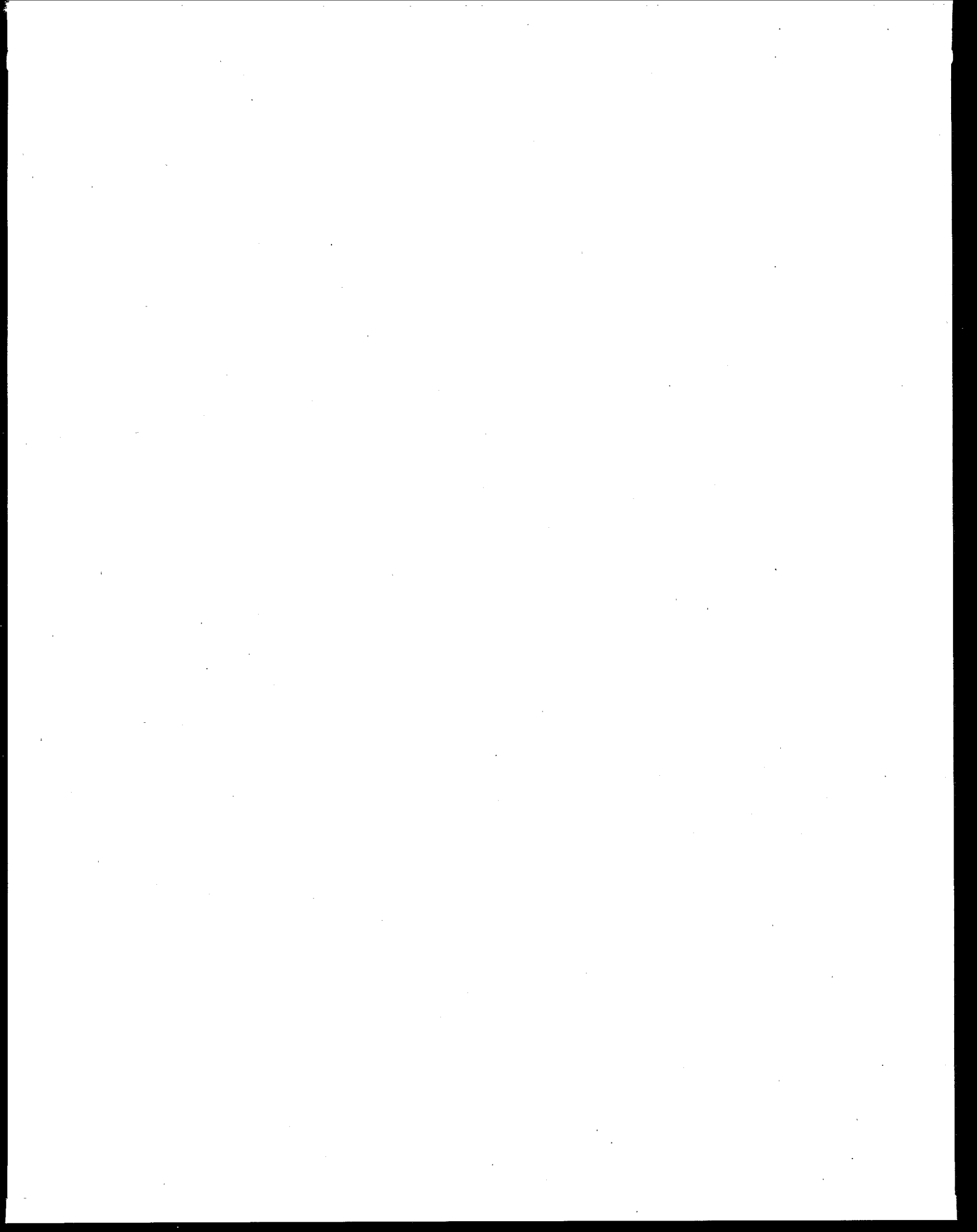
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