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Project Summary

Evaluation of Technologies for *In-Situ* Cleanup of DNAPL Contaminated Sites

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Ground-water contamination by nonaqueous phase liquids poses one of the greatest remedial challenges in the field of environmental engineering. Denser-than-water nonaqueous phase liquids (DNAPLs) are especially problematic due to their low water solubility, high density, and capillary forces arising from interfacial tension between the DNAPLs and water. As a result, conventional pump-and-treat technologies have met poor success in remediation of DNAPL-contaminated aquifers. In certain situations, conventional pump-and-treat methods may actually extend existing contamination into previously uncontaminated areas. The problems associated with current pump-and-treat remedial approaches have served as the impetus to develop alternative technologies to accelerate *in-situ* DNAPL contamination remediation. This report provides a review and technical evaluation of *in-situ* technologies for remediation of DNAPL contamination occurring below the ground water table. Various *in-situ* technologies are reviewed and are evaluated on the basis of their theoretical background, field implementation, level of demonstration and performance, waste, technical and site applicability/limitations, and cost and availability.

This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering Information at back).

Introduction

This report assesses *in-situ* treatment technologies as they pertain to the treatment, mobilization, and recovery of DNAPLs from the subsurface. It identifies *in-situ* technologies that remediate DNAPLs below the water table; secondary importance is placed on contaminants dissolved in the aqueous phase. Remedial options are controlled by technology evaluation and selection, site considerations, regulations, cost, extent of contamination, and presence of other waste types.

DNAPL Fate and Transport Processes

A DNAPL is a sparingly soluble hydrocarbon having a specific gravity greater than that of water at a typical soil temperature, usually less than 20°-25°C. The distribution of a DNAPL within the subsurface results from chemical and physical interactions among the DNAPL, pore water, pore gases, and porous media. Four phases can be present in the subsurface: the gas phase (in the vadose zone); the solid phase (rock, soil grains, soil organic matter); the aqueous (polar) phase; and the DNAPL (nonpolar phase). For the DNAPL to migrate as a separate phase in any direction, both the capillary pressure resisting DNAPL flow and the DNAPL retention capacity of the soil must be exceeded.

The report predicts how hydrophobic compounds will partition in a complex subsurface environment, and to what extent *in-situ* technologies will affect partitioning. Two classes of equilibria problems exist: (1) those where only sparingly soluble hydrocarbons are present, in which the objective is to predict the evolution of the composition of the multicomponent nonaqueous phase liquid pool over time, considering all partitioning that may take place; and (2) those where natural or synthetic surfactants or hydrophilic organic solvents

such as alcohols, ethers, ketones, amines, nitriles are also present, in which the objective is to predict their influence on the resulting chemical equilibria.

Injection, extraction, observation wells, other invasive monitoring, sampling, and remedial structures locally disrupt the stratigraphy and therefore introduce bias. Sampling data can often be misleading relative to the nature and extent of contamination, principally in the delineation of DNAPL in the subsurface. Frequently the importance of multicomponent-multiphase equilibria and interphase transport phenomena has been ignored or underestimated.

Soil heterogeneity affects DNAPL fate and transport. The site stratigraphy affects the distribution of the DNAPL in the subsurface, and the contaminant distribution then plays a critical role in the selection of the overall approach for site remediation. Ultimately, the success of any passive or active in-situ technology is largely associated with its susceptibility to soil heterogeneities and its ability to favorably alter the DNAPL properties to facilitate recovery or remediation.

Successful technologies also have to be able to adapt to other site-specific conditions such as depth to the water table, depth of the contaminated zone, volume of contaminated soil, site access, and manmade structures.

Remedial goals often require that a baseline aqueous contaminant concentration be attained or that in excess of 99% of the DNAPL be treated or recovered. This standard poses a challenge to many technologies.

Technology Evaluation

Several of the evaluated technologies were not originally developed for remediation of contaminated sites, much less DNAPLs. As a result, some of the technologies have not yet been demonstrated on DNAPLs, and, owing to their developmental stage, have not been demonstrated in the field below the water table. Some in-situ technologies that have potential applicability to remediation of DNAPLs occurring below the water table have been demonstrated in the vadose zone only. However, the evaluation of technologies used to clean up contamination in the vadose zone is not included in this report. Also, several in-situ technologies have been fully demonstrated only in non-environmental applications and are currently being adapted for environmental applications. In all cases, the applicability to remediation of DNAPLs occurring below the water table is nonetheless considered.

Biological Processes

In-situ biodegradation is a process in which aqueous phase organic compounds are completely or partially metabolized by microorganisms situated in the subsurface. Bacteria are largely responsible for the biological transformations that occur in porous media and are generally considered as a stationary phase either through attachment to solid surfaces or via agglomeration. These organisms convert natural and xenobiotic organic compounds into energy and end products and use a portion of the organic material for cell synthesis.

Metabolic processes of aerobic and anaerobic microbial consortia are distinguished by the nature of carbon substrate use, and three metabolic processes are recognized: primary metabolism, secondary metabolism, and cometabolism. The metabolic use of a compound depends on its molecular structure, concentration, environmental conditions, bioavailability of nutrients, presence of competing or inhibitory substrates, the nature of the microbial consortia and the enzymes and cofactors they possess, and toxicity effects.

Primary metabolism of an organic compound occurs when it

- yields sufficient energy for cell maintenance and growth and
- is present at concentrations large enough to sustain the microbial population.

Petroleum hydrocarbons are good examples of primary substrates, while compounds such as ammonia can serve as a primary energy source but not a carbon source. Many stoichiometric relationships describing the oxidation and reduction of organic compounds by microbes are known. From the stoichiometric relations, nutrient demands can be estimated and Monod kinetics can be used to relate the growth and decay of the microbial consortia to the degradation reactions.

Secondary metabolism describes the use of trace organic compounds that cannot sustain microbial growth. Cometabolism occurs when nonspecific microbial enzymes or cofactors biotransform organic compounds that provide insignificant energy and organic carbon for growth. Cometabolism is one of the major mechanisms in the transformation of chlorinated hydrocarbons and pesticides.

Electrolytic Processes

In-situ electrolytic processes use applied electric fields to enhance organic contaminant removal. The effectiveness of these processes in soils is controlled by coupled flow phenomena. Usually the flow results from the presence of fluid, heat, electrical, and chemical flow potentials; any of these potentials may be created even though only one driving force is applied.

Containment and Ground Modification

Containment systems and ground modification methods are used to contain and immobilize dissolved contaminants and, in certain cases, DNAPLs. Containment systems are usually placed on the periphery of the contaminated area so that the encompassed area becomes isolated from its surroundings. Impermeable barriers and ground-water injection/extraction systems are examples of containment systems. The ground modification methods are usually confined to DNAPL source areas and immobilize or neutralize the contaminants. Stabilization/solidification (S/S), vitrification, and permeable treatment walls are examples of ground modification. Containment and ground modification can be either passive or active; the distinction is made on the required energy expenditure after installation.

Immobilization of contaminants is achieved by neutralization, precipitation, sorption, and physical encapsulation of the contaminants within a solidified soil matrix. The major issues surrounding in-situ S/S are chemical compatibility and the durability and leachability of the treated soil mass.

In-situ permeable treatment walls are granular backfill walls that provide treatment of dissolved contaminants but no containment or immobilization. The composition of the porous backfill can promote favorable conditions for in-situ biodegradation, precipitation, and chemical oxidation or reduction. The major issues regarding in-situ permeable treatment walls pertain to changes in ground-water flow direction, clogging, long-term performance, and incomplete treatment of wastes.

Soil Washing Processes

In-situ soil washing (or fluid flushing/flooding) relies on fluid-fluid displacement processes to enhance contaminant removal. Fluids can be injected into the porous media to mobilize the resident pore fluids, water, and DNAPL. This is done by a combination of physical forces that can

be aided by favorably altering chemical partitioning so that bulk fluid properties change. The exact nature of the displacement and the prevailing physical and chemical behavior occurring in these systems depends on the liquid properties and environmental conditions.

Air Stripping Processes

In-situ air stripping processes rely on the air circulation through the subsurface to remove volatile DNAPLs from the subsurface. The applications considered here, in-situ air sparging, vacuum extraction, and vacuum vaporizer wells, differ from conventional air stripping and soil vapor extraction in the vadose zone in that they operate in both the saturated and unsaturated zones.

Air sparging and vacuum extraction entail the injection of clean air directly into the saturated zone. Stripping occurs in the porous medium, and volatilized contaminants are recovered by vapor extraction wells nested in the vadose zone. Vacuum vaporizer wells, or UVBs, create water recirculation cells in the porous media. Stripping is performed "in-well," and contaminant-laden vapors are collected at the top of the well. Water is recycled back into the aquifer. UVBs can also simultaneously recover soil vapors from the vadose zone.

Both processes apply to the recovery of volatile and semi-volatile DNAPLs only. Sparging may also result in uncontrolled migration of DNAPL out of the treatment zone. Enhanced biostimulation may be a beneficial byproduct of both processes. Both technologies are commercially available and used.

Thermal Processes

Thermal and thermally enhanced processes deliver thermal energy into the subsurface: the CROW® process uses hot water and/or low quality steam injection; in-situ steam enhanced extraction (SEE) relies on high quality steam injection; and radio frequency heating and in-situ vitrification (ISV) facilitate heating using microwave and electrical arrays, respectively. During these processes, steam and hot water progress through cool porous media and heat the interstitial fluids and porous media. These fluid-fluid displacement processes are analogous to liquid-liquid displacement processes with the added complexity of heat transfer. The contaminants can be recovered as vaporized gases and as dissolved- and separate-phase liquids.

The effectiveness of the CROW® process and SEE is controlled by the thermo-dynamics and hydrodynamics of hot water and steam displacement in porous media. Thus, the thermal properties of both the porous media and the pore fluids become important. The orientation and shape of the propagating steam fronts are governed by the matrix heterogeneities, geometry of the aquifer, initial moisture and boundary conditions, steam quality, injection rates, and the ratio of buoyancy to viscous forces. In saturated homogeneous isotropic porous media, the ratio of buoyancy to viscous forces is important in terms of gravity override and effective sweep-out. The same principles hold for condensation fronts propagating through layered media, but the temperature profiles and fronts will be curved at layer interfaces owing to intrinsic permeability differences. When gravity effects are negligible, the behavior of propagating fronts can be predicted and controlled.

Radio frequency heating achieves subsurface heating by using an electrode array system to transmit electromagnetic waves through the porous media. In-situ moisture is converted to a steam front that propagates through porous media thus displacing other pore fluids, including DNAPLs.

ISV also employs an electrode array system but for the purposes of current flow. Large current flows cause electrical resistance (joule) heating of the soil to the melting point. During this process, DNAPLs can be volatilized and pyrolized.

The CROW®, SEE, and radio frequency heating processes have their origins in the enhanced oil recovery business. ISV was developed for the S/S of wastes containing radionuclides. All of these technologies have been demonstrated at the pilot scale, but only CROW® and SEE have been successfully demonstrated in the saturated zone. A full-scale demonstration of SEE is in progress.

Results and Discussion

This study was conducted between December 1991 and May 1993. No actual experiments were conducted. Approximately 400 references were compiled during this study. Information was collected from journal articles, conference proceedings, vendor and manufacturer fact sheets and literature, and federal, state, and local agency reports and publications. The authors also attended a number of conferences to obtain information that was as current as possible.

To supplement these sources of information, an "In-situ DNAPL Remediation Technology Description Questionnaire" was developed in cooperation with EPA personnel at the Robert S. Kerr Environmental Research Laboratory. The questionnaire was sent to professionals working in the area of DNAPL cleanup. These questionnaires were first mailed in February 1992. Positive responses were followed up with letters and personal contacts. As the project progressed, the correspondence was expanded.

Descriptions of the relevant in-situ technologies were then prepared. The following aspects of each relevant in-situ technology were evaluated: theoretical background, field implementation, level of demonstration and performance, applicability/limitations, and cost and availability. Several technologies have been demonstrated.

Limitations of the Report

The technology descriptions included in the report cannot be considered exhaustive because of the following limitations:

- short time—18 months
- poor literature reporting
- gaps due to unavailability of information
- nature of proprietary research and/or confidential information
- stage of development of technology

Therefore, the expected performance of these technologies can be difficult to interpret in the context of DNAPL cleanup.

While this report can help identify potentially applicable in-situ technologies for cleanup of DNAPL-contaminated sites, it should not be the sole basis for selecting a technology for a particular DNAPL at a given site. The report is not a substitute for engineering judgement, analysis, and design. Potential in-situ technologies must be further evaluated by contacting technology developers and by performing bench- and/or pilot-scale treatability tests as necessary under site-specific conditions. This is especially true for undemonstrated technologies and for technologies whose success depends heavily on the characteristics of the waste matrix.

Conclusions

The remediation of DNAPLs faces challenges posed by the site stratigraphy and heterogeneity, the distribution of the contamination, and the physical and chemical properties of the DNAPL. A successful technology has to be able to overcome the problems posed by the site complexity and be able to modify the properties of the DNAPL to facilitate recovery, immobilization, or degradation. In addition, the

methodology must be adaptable to different site conditions and must be able to meet the regulatory goals.

Thermally based technologies are among the most promising. Among thermal technologies, SEE is probably the most promising candidate. The CROW® process relies on similar mechanisms; however, it is not clear whether the injection of hot water and low quality steam offers an advantage over SEE. Radio frequency heating, which relies on in-situ steam generation to be most effective, has only been tested in the vadose zone.

The next group of promising technologies are the soil washing technologies because they can manipulate chemical equilibria and reduce capillary forces. A blend of alkalis, cosolvents, and surfactants is probably the best combination for a soil washing application, and each is important for its own reasons; alkalis can saponify certain DNAPLs and affect wettability and sorption, cosolvents provide viscous stability and enhance solubility and mass transfer between the aqueous phase and the DNAPL, and surfactants have the largest impacts on solubility and interfacial tension reduction. Water flooding is best applied in highly contaminated areas as a precursor to these methods.

The thermal and soil washing technologies are best suited for areas that are highly contaminated with DNAPLs. However, these techniques by themselves still may not be able to achieve the currently mandated regulatory cleanup standards. Thus, consideration should be given to using these technologies in combination with the technologies suitable for long-term plume management. The bioremediation techniques and permeable treatment walls hold the best promise.

A special problem is posed by mixed wastes, heavy metals and radionuclides mixed with DNAPLs since recovery at the ground surface may not be desirable in many instances. In such instances, S/S and vitrification are the most viable in-situ technologies. Excluding radionuclides, in-situ S/S is the most promising candidate because of its broadly demonstrated effectiveness, cost, and applicability to the saturated zone.

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