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In Situ Treatment of Contaminated Ground Water:

An Inventory of Research and Field Demonstrations and Strategies for Improving Ground Water Remediation

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In Situ Treatment of Contaminated Ground Water: An Inventory of Research and Field Demonstrations and Strategies for Improving Ground-Water Remediation Technologies

Technology Innovation Office
Office for Solid Waste and Emergency Response
U.S. Environmental Protection Agency
Washington, DC

EXECUTIVE SUMMARY

Approximately 75% of the sites on the National Priorities List (NPL) have ground-water contamination. An analysis of the Records of Decision (RODs) for these sites shows that pump-and-treat remediation is almost exclusively chosen as the technology to address this contamination. However, this technology has limited success, depending on the hydrogeologic conditions and the target contaminants. The Technology Innovation Office (TIO) investigated the availability and development of alternate technologies which may replace or enhance pump-and-treat remediation. This paper provides an overview of the findings of this review and suggests strategies to bring more focus and coherence to the research, development, and application of *in situ* ground-water remediation technologies.

CONCLUSIONS

- Alternate technologies to pump-and-treat remediation are extremely limited.
- At the present rate of development, alternate technologies may not be available for 3 to 5 years.
- Fifteen technologies are being developed; however, most are in the bench scale or pilot stages.
- Avenues of development support are available in the SITE Program, EPA labs, or the Hazardous Substance Research Centers.
- Information sharing is efficient within the EPA umbrella, but sporadic between responsible parties and industrial interest groups.
- Information on technology development or demonstration is not easily obtained.

RECOMMENDATIONS

- The development, diversity, and information-sharing concerning ground-water remediation technologies must be improved by all stakeholders.
- Ground-water remediation workshops, conferences, or forums should help the exchange of ideas and experiences.
- Information and data from field demonstrations and applications should be more easily accessible to potential users.
- Demonstration programs should be directed more toward *in situ* ground-water treatment.

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ABSTRACT

The mission of the U. S. Environmental Protection Agency's (EPA's) Technology Innovation Office (TIO) is to stimulate the development and application of innovative treatment technologies at sites contaminated from hazardous wastes and to remove impediments that inhibit the use of such technologies. TIO has become increasingly aware of the difficulties of remediating ground water once it has been contaminated. A recent study has shown that remediation or control of contaminated ground water using conventional pump-and-treat technology is difficult at many sites and, in most cases, incomplete. Consequently, there is a need for improved ground-water remediation technologies. In response, TIO plans to promote the development and field application of alternative technologies to increase the options available.

As a first step, TIO began developing an inventory of treatment technologies either being researched, field tested, or actually demonstrated and used. Sources of information included universities, government research laboratories, private laboratories, and hazardous waste sites where the technologies are actually in use. This inventory includes chemical, biological and physical treatment techniques that either alter the toxicity of the contamination or improve removal. Technologies to improve the mobility of non-aqueous phase liquids are in the scope. However, pumping techniques and the construction of physical barriers are not.

INTRODUCTION

The predominance of ground-water contamination at hazardous waste sites (Figure 1) and the dearth of methods to efficiently treat this contamination is a problem that the U.S. Environmental Protection Agency (EPA) is examining. The contaminated ground water found at most Superfund sites is often the limiting factor for complete site remediation.

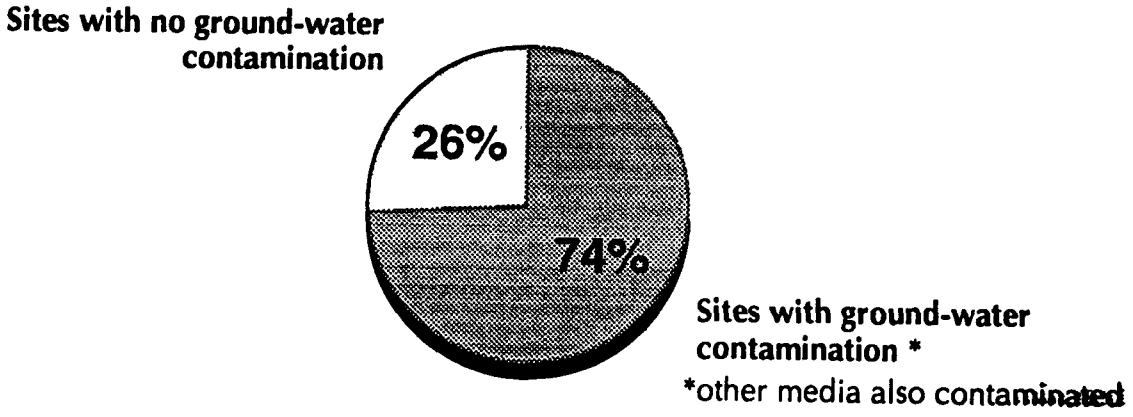

Figure 1. Occurrence of Ground-Water Contamination at NPL Sites

Until recently, many believed that contaminants in surface soils were the only significant source of ground-water contamination. Consequently, development of remediation technologies focused mainly on this source. Ground-water management was limited to pump-and-treat containment while *in situ* ground-water treatment was ignored. Technologies to remediate contaminated ground water *in situ* still are not well developed, primarily because contaminated ground-water plumes are difficult to define, contaminants can migrate in different directions simultaneously, and, in most cases, the subsurface is unreachable for *in situ* physical examination.

Between 1982 and 1991, 70% (306) of all Superfund site Records of Decisions (RODs) addressing ground-water remediation specified pump-and-treat technology for plume containment (Figure 2). Within the past few years, regulators and researchers studying data from pump-and-treat remediation systems have become convinced that, in addition to contaminated soils, the source of much ground-water contamination is dense nonaqueous phase liquids (DNAPLs) and other compounds that migrate downward into aquifers and often form pools of immiscible liquid contaminants in the subsurface. The efficiency of contaminant removal from ground water at sites where DNAPLs are present is contingent on the solubility of the contaminant, efficiency of the pumping system and hydraulic characteristics of the aquifer. Unless the system is directly removing the contaminant source, pump-and-treat systems only contain contamination. Since most organic contaminants are, at best, sparingly soluble in water, achieving remediation goals will be a long, inexact and expensive process. This recognition is fueling an increased interest in improving the efficiency of pumping systems as well as in *in situ* treatment of contaminated ground water and subsurface contaminant sources.

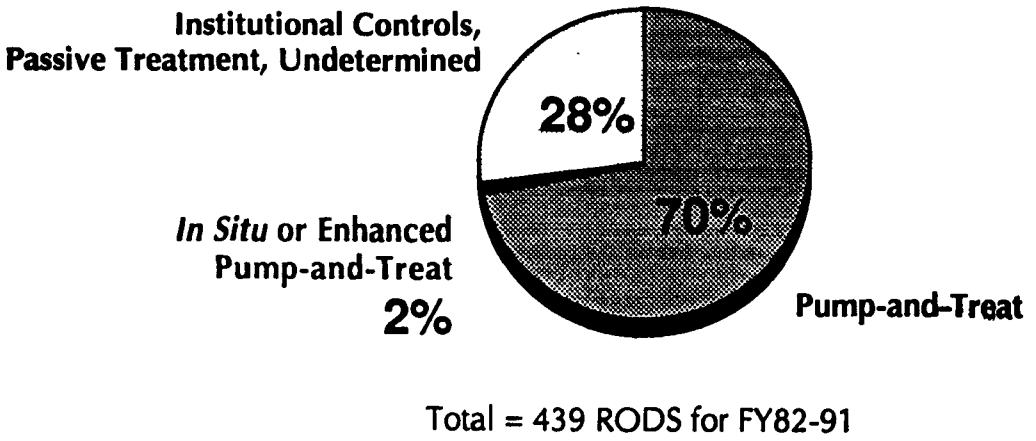

Figure 2. Treatment Specified in Ground-Water RODs

The purpose of this document is to describe recent research, development and application of technologies that either treat ground-water contaminants in place or improve the solubility and mobility of contaminants to enhance pump-and-treat remediation effectiveness. This report discusses techniques that can be applied *in situ* and excludes pumping methodologies or surface treatment systems. Figure 3 illustrates the status of research and demonstration for the treatment techniques discussed in this report. Figure 4 shows the status of research and demonstration for enhanced recovery techniques. In addition, this publication presents conclusions based on observations of the survey. Finally, strategies for action for stakeholders concerned with *in situ* ground-water technology development are presented. This study has not defined the extent or activities of research and development outside of EPA-supported groups.

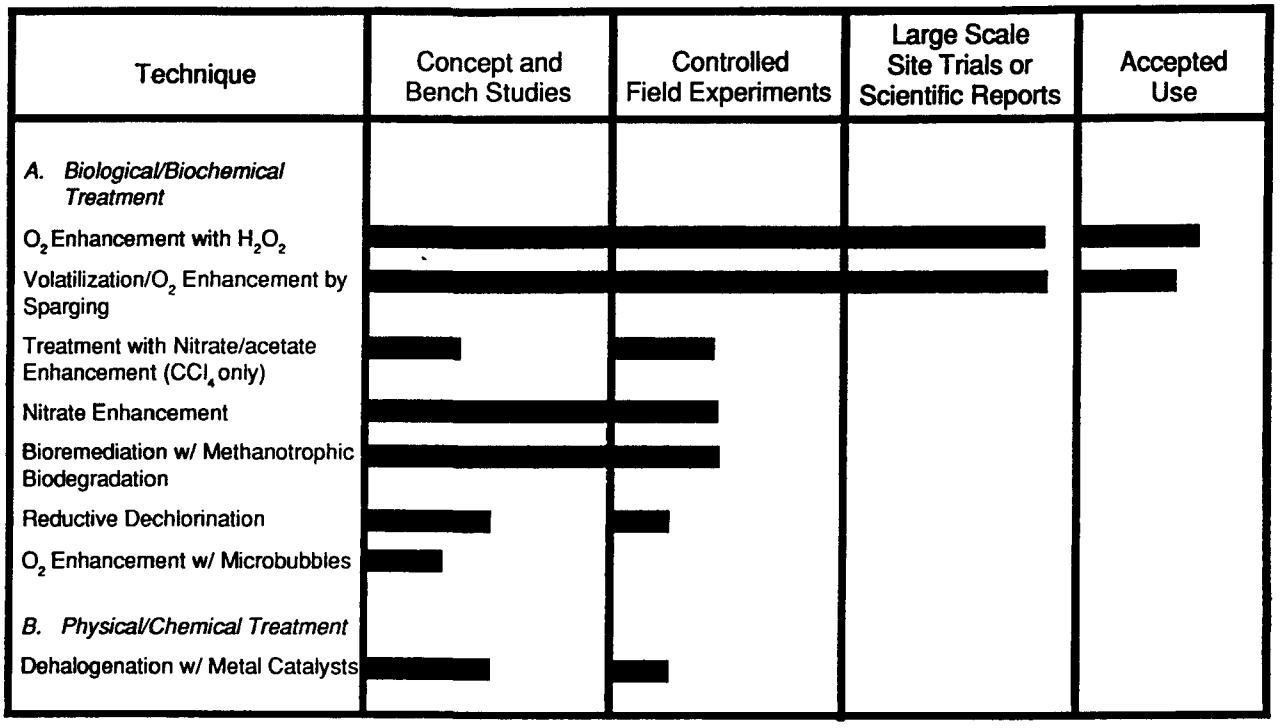

Figure 3. Status of Research and Demonstration Projects for Treatment

KEY

Concept and Bench Studies: Theoretical models are developed and information searches conducted. Bench and column studies are conducted in the laboratory. Most experimental variables (temperature, water content, contaminant concentration) are controlled.

Controlled Field Experiments: Studies are conducted on field plots and many of the variables are uncontrolled. Contaminant concentrations, however, are usually controlled and adjusted. Data are used to calibrate generic predictive models.

Large Scale Site Trials: The technology is applied under actual site conditions with uncontrolled variables. Data collection and analysis is comprehensive and used to refine the site predictive model.

Accepted Use: The technology is used for site cleanups and cost and performance data are being obtained. A description of the technology is included in general guidance for site cleanups. Generic predictive models are available.

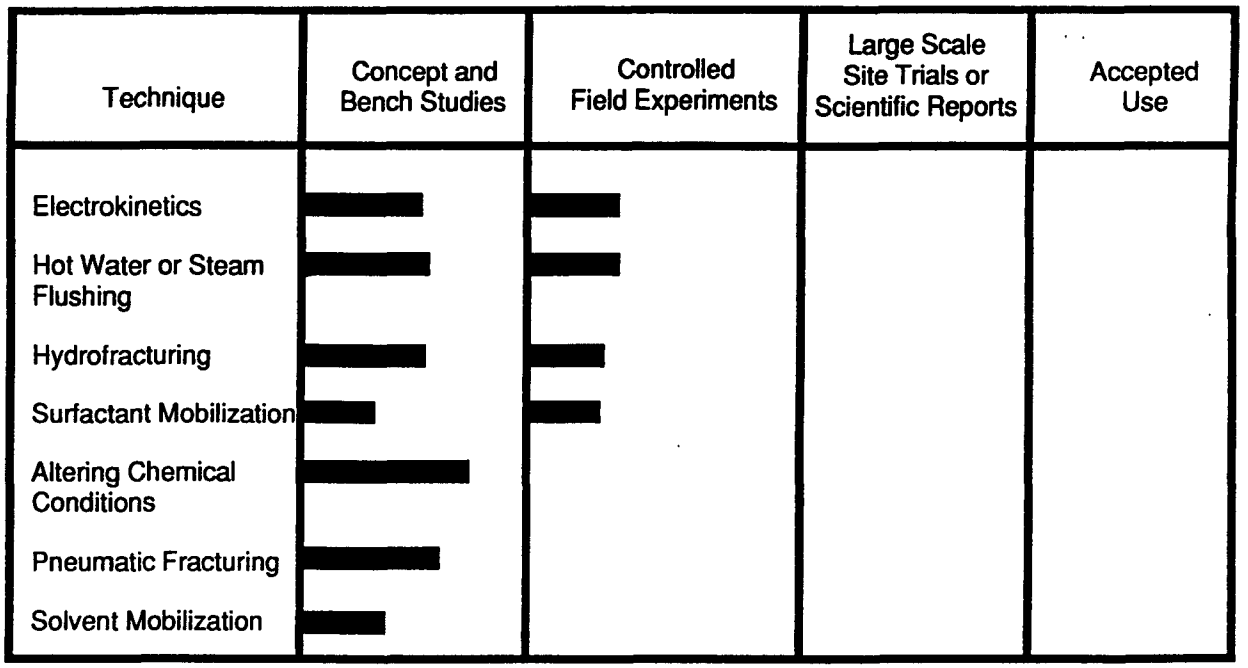

Figure 4. Status of Research and Demonstration Projects for Enhanced Recovery

Information on the innovative treatment technologies in this report was found in computerized hazardous waste information databases such as EPA's Alternative Treatment Technologies Information Center (ATTIC) Database, Hazardous Waste/Superfund Database, ORD Bibliographic Database and Records of Decision System (RODS). The Ground Water Network of the National Ground Water Information Center was also consulted. The review also included EPA research descriptions, conference summaries, proceedings and compendiums. The survey was supplemented with personal interviews and discussions with representatives of other federal agencies, academic research centers and hazardous waste remediation consulting firms.

DESCRIPTION OF TECHNIQUES

Contaminant Treatment: Biological/Biochemical Methods

Oxygen Enhancement with Hydrogen Peroxide. Refined petroleum can be readily biodegraded under aerobic conditions; however, the rate of biodegradation is limited by the relatively low solubility of oxygen in water. This problem can be overcome by injecting hydrogen peroxide. In the most common application, a dilute solution of hydrogen peroxide is injected into contaminated ground water.

This is an accepted technology often used in EPA's Underground Storage Tank (UST) program. Variations, including the addition of nutrients to the hydrogen peroxide solution, are used if site conditions permit. Field experience has shown that while the oxygen it provides is beneficial, hydrogen peroxide itself is toxic to microorganisms. Consequently, its use must be carefully monitored. The cost of hydrogen peroxide compared to that of oxygen must also be considered.

Researchers from EPA's R. S. Kerr Environmental Research Laboratory (RSKERL) in Ada, Oklahoma, are in the process of obtaining performance and cost data from the Bioremediation Performance Evaluation Project at the Champion International Superfund Site in Libby, Montana. Another RSKERL research project that was carried out for several years in cooperation with the Traverse Group and Rice University (National Center for Groundwater Research) at a U.S. Coast Guard Station in Traverse City, Michigan, has produced some of the best data available on the process. Additional research is being conducted at the EPA-sponsored Great Plains and Rocky Mountain Hazardous Substance Research Center.[1]

Volatilization/Oxygen Enhancement by Air Sparging. Sparging or injection of air under pressure through soils to below the water table can remove volatile organic chemicals (VOCs) by creating a subsurface air stripper. Air bubbles contact dissolved/adsorbed-phase contaminants and non-aqueous phase liquids (NAPLs) in the aquifer increasing volatilization. The volatile organics are transported by the air bubbles into the vadose zone where they can be captured by a vapor extraction system or, where permissible, allowed to escape to the atmosphere. As a bonus, addition of the sparged air creates high oxygen levels in the ground water and vadose zone and enhances natural biodegradation. This technology appears to have been taken from concept to application without significant laboratory research. Estimates are that, at any one time, 25 sites (mainly UST sites) use air sparging techniques.[2]

Ground-water aeration is reported to be a standard procedure in Germany and has been used since 1985. The "UVB technique," a method of air sparging combined with ground-water circulation, has been used at approximately 60 sites in Germany. Contaminated ground water is stripped by air in a below-atmospheric-pressure field. Pumps circulate ground water vertically within the capture zone.

Treatment with Nitrate/Acetate Enhancement (CCl_4 only). Approximately 10 years ago, researchers at the University of Illinois observed that complete chemical breakdown of carbon tetrachloride occurred in columns of soils that also contained acetate and nitrate. In contrast to reductive dechlorination, this reaction produced no chlorinated organic by-products from the degradation of carbon tetrachloride.

Field experiments conducted at the Moffett Naval Air Station by Stanford University through the Western Region Hazardous Substance Research Center and RSKERL have not duplicated the laboratory results. Therefore, at this time, the usefulness of this method is undetermined. By more thoroughly understanding the laboratory results, researchers hope to design a more effective field study.

Nitrate Enhancement. Oxygen-enhanced bioremediation has been effective for many fuel spills. Unfortunately, success is sometimes limited by the low solubility of oxygen. Nitrate can serve as an electron acceptor in a reducing environment. It is more soluble and less expensive to inject

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[1]Wilson, John. 1991. USEPA/RSKERL. Personal communication.

[2]Brown, Richard A., Ph.D. 1991. Groundwater Technology, Inc. Personal communication.

into ground water. However, nitrate is subject to a drinking water standard and its release in the subsurface must be rigorously monitored.

A field demonstration using this technology on a spill of JP-4 jet fuel was conducted in 1991 by RSKERL at a U. S. Coast Guard Station in Traverse City, Michigan. Nitrate was mixed into pumped ground water and reinfiltrated through a subsurface gallery. The performance of this technology was compared with two other *in situ* ground-water treatment technologies at the site: oxygen enhancement with hydrogen peroxide and bioventing by air injection in the vadose zone. All three techniques successfully reduced benzene to below the drinking water standard. Additional EPA-sponsored lab and field-testing is also being conducted at the Western Region Hazardous Substance Research Center.

Bioremediation with Methanotrophic Biodegradation. Chlorinated solvents and their transformation products are the most prevalent priority contaminants found in ground water at Superfund sites. They include trichloroethylene (TCE); 1,1-dichloroethylene (1,1-DCE); 21,1,1-trichloroethane (TCA); 1,2-dichloroethane (DCA); and vinyl chloride (VC). These chemicals are characterized by their relatively high mobility in ground water and their resistance to biological degradation. However, in recent years biodegradation of chlorinated solvents with concentrations less than 100 parts per million has been demonstrated both in the presence and absence of oxygen. (Higher concentrations of chlorinated solvents seem to be toxic to the microorganisms.) However, when certain microorganisms are provided with methane for energy and growth, these methanotrophic organisms produce enzymes that transform chlorinated compounds. Patented by a RSKERL scientist in 1985, the process of providing one chemical to the microorganisms to facilitate transformation of another, called cometabolism, offers new possibilities for environmental restoration.

Laboratory studies on this technique have been conducted through RSKERL, the Northeast Hazardous Substance Research Center, the Western Region Hazardous Substance Research Center and the Biosystems Technology Development Program. A successful field demonstration was conducted by the Western Region Hazardous Substance Research Center at Moffett Naval Air Station, in Mountain View, California. In 1990, the Center also conducted an initial feasibility study for full-scale application at the Allied Signal Corporation Superfund site in St. Joseph, Michigan. (The results of the latter study showed that concentrations of TCE were too high to support methanotrophic organisms and, instead, biodegradation using indigenous microorganisms will be studied.)

ABB Environmental Services, Inc., will demonstrate this technology in the SITE Emerging Technology Program. They propose to treat a mixture of chlorinated and non-chlorinated organic solvents in ground water by applying an *in situ* two-zone plume interception treatment system. The first zone is anaerobic where growth of methanogenic bacteria is stimulated. This zone promotes the reductive dechlorination of chlorinated solvents from highly chlorinated forms such as tetrachloroethylene (PCE), TCE and TCA to less chlorinated forms such as DCE, VC and DCA. The second zone is made aerobic by introducing oxygen. Here the methanotrophs growing on injected methane are expected to oxidize the partially-dechlorinated products from the first zone.

Reductive Dechlorination. Researchers have been studying the isolation and stimulation of indigenous microorganisms capable of dechlorinating polychlorinated biphenyls (PCBs) and other chlorinated hydrocarbons. They have found that changing the environment of the contaminated zone from anaerobic to aerobic is productive. The heavily-chlorinated compounds are dechlorinated in an anaerobic environment and the less heavily-chlorinated compounds can be degraded in aerobic conditions. Theoretically, oxygen-rich water can be pumped into contaminated ground water that is naturally anaerobic. Researchers at some institutions have found, however, that making the system aerobic stimulates the degradation of the less chlorinated daughter products, but also stops the reductive dechlorination of the original, more chlorinated, compounds. EPA is also sponsoring research to develop engineered microorganisms capable of anaerobic reductive dehalogenation.

The feasibility of sequential anaerobic-aerobic treatment of PCB-contaminated sediments is being investigated at the University of Michigan. So far, successful batch experiments have illustrated the potential of the process for *in situ* PCB degradation. With support from the Great Lakes and Mid-Atlantic Hazardous Substance Research Center and General Electric, a large river model will be used to demonstrate the feasibility of the sequential process in a bench-scale study that simulates natural conditions.

An aerobic PCB biodegradation experiment was conducted by General Electric at Fort Edwards, New York, on the Hudson River. General Electric is also planning an anaerobic dechlorination field study on river and pond sediments contaminated with PCBs. Results of the first test will be available in early 1992; data from the second in 1993.[3]

ABB Environmental Services, Inc., proposes to use reductive dechlorination with methanogenic bacteria in a passive ground-water remediation project in the SITE Emerging Technology Program.

Oxygen Enhancement with Microbubbles. This technology is designed to carry oxygen and other nutrients to subsurface microorganisms to stimulate *in situ* bioremediation of organic contaminants in ground water. Oxygen is mixed with an inexpensive, biodegradable surfactant to produce highly stable microbubbles in the 40-per-micron size range. Bubbles this size can remain dispersed in a coarse sand matrix in the saturated zone without significant coalescence.

Partially supported by EPA and the Air Force, researchers at Virginia Polytechnic Institute and State University (Virginia Tech) in Blacksburg, Virginia, have taken the lead in developing this technology. In proposed field tests, microbubbles will be added to the soil either through a laminated interceptor trench perpendicular to the ground-water flow, or through a series of injection wells. As the ground water passes by or through the injected microbubbles, oxygen will slowly dissolve in the water, delivering oxygen to support bacterial activity. Numerous pilot scale studies have been conducted and the developer will perform additional laboratory studies prior to field testing.[4]

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[3]Abramowitz, Dan. 1991. General Electric. Personal communication.

[4]Michelsen, Don. 1991. Virginia Polytechnic Institute. Personal communication.

Contaminant Treatment: Physical/Chemical Methods

Physical/chemical methods of contaminant treatment have not been studied as extensively as biological methods. There has been little field testing to date. Many physical/chemical treatment techniques lend themselves to use in above-ground reactors but few to *in situ* use because of the difficulties in achieving effective contact of a catalyst with contaminants.

Dehalogenation with Metal Catalysts. Researchers are studying the use of metal catalysts in the degradation of halogenated organic compounds in aqueous solutions. Based on batch and column tests, the catalyst performs two functions: (1) it produces highly reducing conditions, and (2) it participates in the degradation process. The catalysts have been effective in degrading a range of halogenated methanes, ethanes and ethenes.

Investigators conducted a small-scale field test using iron filings as the treatment catalyst at the Waterloo Center for Groundwater Research in Ontario. They placed permeable walls containing the catalyst underground perpendicular to the flow of contaminated ground water. The system is entirely passive and cost effective—the catalyst is even an industrial waste product. Seventy percent of the organic compounds present (trichloroethylene and carbon tetrachloride) were removed. The lack of complete degradation was believed to be the result of cutting oil residue on the iron filings. The Waterloo Center continues to conduct laboratory work on this technique.[5]

The University of Michigan has developed chemical model systems to study the extent to which transition metal-organic catalysts influence the rate of dechlorination of chlorinated aliphatic compounds.

Enhanced Contaminant Recovery

The terms "removal by pumping" and "pump-and-treat" refer to the extraction of contaminated ground water and subsequent treatment of the extracted ground water at the surface. Extraction is accomplished through the use of extraction (pumping) wells operated at specific locations and depths to optimize contaminant recovery. Injection wells may be installed to enhance recovery by flushing contaminants toward extraction wells. This technology is best suited for managing mobile chemicals found in relatively permeable and homogeneous hydrogeologic settings. The techniques described below are designed to improve the effectiveness of pump-and-treat systems.

Electrokinetics. When an electric field is applied to a porous material containing a liquid (soil, for example), movement of charged molecules and of the liquid itself is induced. The phenomenon is known as "electroosmosis." As the electric field pulls positively charged ions toward the cathode, the water in the pores is also drawn toward the cathode due to "viscous drag." Consequently, positively-charged organic or inorganic contaminants can be made to migrate in the electric field to a collection point for removal by pumping.

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[5]Gillham, Robert. 1991. University of Waterloo. Personal communication.

Two major laboratory efforts are providing information on this technology. Research at the University of Colorado is currently funded by the Electric Power Research Institute and has been funded in the past by the U.S. Air Force. Experimental results show elevated concentrations of contamination in water adjacent to the electrodes. Researchers at Massachusetts Institute of Technology (MIT) have been studying electrode emplacement geometries and electric field strengths under a grant from the Northeast Hazardous Substance Research Center.Commercial application of electromigration in Europe has been led by a company called Geokinetics in Rotterdam, The Netherlands. Some of their laboratory and field tests report a wide range in the removal levels of heavy metal. Success appears contingent on hydraulic conductivity. The highest degree of removal, over 90%, was achieved in clayey soils, whereas in porous soils only 65% was removed.

In the United States, Electrokinetics, Inc., will conduct studies under the SITE Emerging Technology Program. Bench-scale laboratory studies investigating the removal of heavy metals, radionuclides and organic contaminants will be completed by the end of 1991. Field studies investigating removal of radionuclides will be completed in late 1992. The technology will be available for full-scale implementation upon completion of the pilot-scale studies.

Hot Water or Steam Flushing. This process removes volatile and semi-volatile organic compounds such as TCE, TCA and dichlorobenzene (DCB) above and below the water table. Steam is forced into the aquifer by injection wells and the vaporized volatile components are removed by vacuum extraction. The technology uses readily-available components, such as extraction and monitoring wells, manifold piping and vacuum pumps. Hot water injection may be particularly useful at oil refineries, which often have oil-contaminated ground water and waste heat that can be used in the recovery process.

Udell Technologies, Inc., completed a successful demonstration of steam-enhanced extraction in 1988 and the technology is now scheduled to be demonstrated under the SITE Demonstration Program at the McClellan Air Force Base in Sacramento, California. The site is contaminated by waste oils mixed with VOCs, semi-volatile organic chemicals and metals.

A case study will be performed by the Department of Energy to remediate a gasoline spill to depths of 137 feet at the Lawrence Livermore National Laboratory in Livermore, California. The Naval Civil Engineering Laboratory, in Port Hueneme, California, and EPA's Risk Reduction Engineering Laboratory (RREL) in Cincinnati are also considering a demonstration at the LeMoore Naval Air Station.

A similar use of thermal technology can be used to recover oily wastes by adapting a technology presently used for secondary petroleum recovery and for primary production of heavy oil and tar-sand bitumen. Steam is injected below the oily wastes and condenses to cause rising hot water that dislodges the oils upward into more permeable soil regions. Hot water can then be injected adjacent to the now-floating oil bank to move the oil to extraction wells as it is contained and moved by barriers of hot water. *In situ* biological treatment may follow the displacement. It can be applied to manufactured gas plants, wood treating sites and other sites with saturated soils containing organic liquids such as coal tars, pentachlorophenols, creosotes and petroleum by-products. The Western Research Institute (WRI) has tested this technology in the laboratory and in a field study under the SITE Emerging Technology Program. In the SITE Demonstration

Program, WRI will conduct additional studies at the Pennsylvania Power and Light Brodhead Creek Site in Stroudsburg, Pennsylvania. In addition to the SITE Program demonstration, the technology is now being demonstrated at a wood treatment site in Minnesota.

Hydrofracturing. Hydrofracturing involves the cracking of low permeability and over-consolidated sediments using pressurized water injected through wells. The resulting cracks are filled with a porous medium such as a sand/gel mixture that props open the cracks to form sand-filled lenses that serve either as avenues for bioremediation or to improve pumping efficiency. Three hydrofracturing field demonstrations on VOCs in the unsaturated zone have been conducted by RREL—two combined with vapor extraction and one with bioremediation. The developers believe that it can be used in the saturated zone as long as the sediments can be fractured. RREL is ready to apply the technology to any site that meets the geologic criteria.

Surfactant Mobilization. Surfactants increase contaminant mobility in two ways. The first is by increasing the solubility of the contaminant in water. This speeds up the removal of sorbed contaminants by increasing their concentration in solution. The second is by reducing interfacial tension of nonaqueous phased liquids (NAPLs). This requires greater surfactant concentrations than those required for increasing solubility, but results in direct mobilization of the NAPL, which may allow it to be extracted more efficiently. Although the successful application of surfactants to enhance oil recovery has been demonstrated, transferring the knowledge to problems of aquifer remediation is not direct. Incorrect formulation and application can exacerbate remediation by making the NAPL more mobile thereby increasing its potential to reach larger populations as it flows in the subsurface.

Surfactants can effectively complex and exchange with metal ions. Investigators in the laboratories at the University of Oklahoma have demonstrated the use of cationic surfactant polymers for separation of anionic contaminants such as chromate from aqueous solution through selective binding. Laboratory studies at RSKERL have shown that anionic surfactants increase the removal efficiency of adsorbed chromate from aquifer sediments. Researchers at the Great Lakes and Mid-Atlantic Hazardous Substance Research Center have developed computer and physical models of surfactant mobilization systems. The Western Region Hazardous Substance Research Center is studying the use of surfactants to improve biodegradation. Researchers at the State University of New York-Buffalo are conducting field tests on surfactant mobilization of PCE at the Borden Canadian Forces Base (with scientists from the Waterloo Center) and of carbon tetrachloride at the Dupont Chemical Plant in Corpus Christi. Studies will continue until mid-1992. Researchers at Rice University (National Center for Groundwater Research) are studying methods to increase the amount of natural surfactant produced *in situ* by subsurface microbial populations. Much of the research conducted has been concerned with the efficiency of surfactants to solubilize, but little has been done concerning the fate and behavior of these compounds.

Altering Chemical Conditions. Changing the redox conditions in aquifers theoretically can change the valence state of a metal contaminant in ground water. This can reduce its mobility or make it less toxic, such as in the transformation of hexavalent chromium to trivalent chromium. Scientists at the Western Region Hazardous Substance Research Center and EPA's Environmental Research Laboratory in Athens, Georgia (AERL) have conducted laboratory tests

on reducing hexavalent chromium in aquifer materials. AERL researchers are now ready to study this technology in a field test.

Shifting the equilibrium solubility of solids and solid/solution systems can change the aqueous concentrations of some contaminants. The Oregon Graduate Institute is exploring chemical enhancement with barium sulfate for a pump-and-treat operation at a chromium-contaminated site. At sites with extensive chromium contamination, a large fraction of the chromium appears to be precipitated in a solid barium chromate phase from which it slowly dissolves into ground water. The slow rate of dissolution limits the rate at which the chromium can be pumped from the aquifer. Adding barium sulfate will increase the solubility of the chromate by substituting sulfate for chromate in the solid phase. This technology is still at the laboratory bench-scale stage.

Pneumatic Fracturing. This process requires the injection of highly pressurized air into the subsurface contaminated zone to extend existing fractures and create a secondary network of fissures and channels. This enhanced fracture network increases the permeability of the soil to liquids and vapors and accelerates the removal of contaminants, particularly by vapor extraction, biodegradation and thermal treatment.

The New Jersey Institute of Technology (NJIT), with support from the Northeast Hazardous Substance Research Center, conducted studies of pneumatic fracturing as part of the SITE Emerging Technology Program beginning in 1988. Four field demonstrations all showed an improved permeability in relatively impermeable soils and rock. To date, most of the work on this technology has been in the unsaturated zone but the NJIT developers believe that the removal of contaminated ground water can also be enhanced by pneumatic fracturing.

In 1990, this technology (integrated with a surface treatment system) was accepted in the SITE Demonstration Program. Accutech Remediation Systems, Inc., will begin their demonstration in 1992 at a TCE-contaminated site in New Jersey.

Solvent Mobilization. The rate of removal of organic contaminants is often limited by their low solubility in water. Many of these contaminants are much more soluble in solvents other than water. Although theoretical models suggest that the injection of solvents into a contaminated zone can improve mobility of several organic compounds, complications in the field include complex and unpredictable transport behavior, biofouling of the aquifer and reductive dissolution of iron and manganese oxides that clog wells.

Laboratory experiments on solvent mobilization have been conducted by researchers at the Northeast Hazardous Substance Research Center, but no field studies have been completed. Researchers at RSKERL are conducting laboratory tests and, in cooperation with the U.S. Coast Guard, expect to begin a small-scale field test of solvent flushing at Traverse City in 1992.

CONCLUSIONS

Research Coordination

1) **EPA has provided avenues for development of *in situ* ground-water remediation technologies through the SITE Program, the Hazardous Substance Research Centers (HSRCs) or directly through the EPA labs.**

   EPA's Office of Research and Development (ORD) has established programs to support the laboratory development and field testing of emerging technologies. Of the 15 technologies examined, five are being studied by researchers at either RSKERL, RREL, or AERL. One patent for *in situ* ground-water treatment has been awarded to a RSKERL scientist. Four of the HSRCs are supporting studies on eight technologies. Two Centers (the Great Lakes/Mid-Atlantic and the Western Region Centers) have committed approximately one third of their grant budget to *in situ* ground-water remediation.

   The Superfund Innovative Technology Evaluation (SITE) Program has accepted five technologies for demonstration and testing—three in the Emerging Technology Program and two in the Demonstration Program. Technology developers may not be aware of these avenues or may choose not to use them. Major stakeholders (refineries, wood treating facilities, electric power generators, etc.) may be supporting development, but information and data from these findings may not be freely distributed.

2) **Communication and information-sharing among EPA-sponsored researchers appears to be efficient.**

   Although the scope of this project did not include process analyses, we observed that the researchers, in most cases, were very familiar with the work of their colleagues. The ORD laboratories, HSRCs and other university-based research centers seem to be the focal points for ground-water research. While EPA researchers are individually informed on their colleagues' work in other federal agencies, there is no centralized sharing or formal networking of research information. Our interviews and literature reviews rarely led to work being supported by responsible parties or industrial interest groups. Communication could be improved between these parties and EPA.

3) **There are no major mechanisms available to collect and distribute information from field demonstrations and applications. The exception are projects involved in the SITE program.**

   We found very little cost and performance data on the two technologies that have reached the stage of "accepted use" (oxygen enhancement by air sparging and hydrogen peroxide injection). Users of these technologies (mostly in the UST Program) explained successes and failures when interviewed, but there is no systematic effort to collect, organize and distribute the data. Six Superfund Records of Decision (RODs) include *in situ* ground-water remediation (five specify nitrate enhancement), but plans to collect data and exchange information concerning experiences during these applications must be developed.

Communications could be improved among managers of Superfund sites that are using similar technologies. We located a developer using the same technology as specified in two RODs on a State-lead cleanup through a chance conversation at a technical conference. The experiences of these developers should be shared among themselves as well as with potential future users.

Technology Status

1) The alternatives to pump-and-treat remediation are extremely limited.

With the exception of oxygen enhancement by sparging and hydrogen peroxide injection, no technology has adequate field demonstration or actual application data to be considered as an alternative to pump-and-treat remediation. Cumulatively, the UST, CERCLA and RCRA programs estimate that 100,000 to 200,000 sites have ground-water contamination. However, only 15 technologies are being developed to supplement or improve pump-and-treat remediation.

2) At the present rate of development and field demonstration, alternative technologies to pump-and-treat remediation may not be available for application for at least 3 to 5 years.

Most of the technologies are approaching, or are in, the "controlled field experiment" stage of development. At this stage, studies are conducted in a natural environment but many factors, such as contaminant concentration and homogeneity, are controlled and adjusted. Laboratory and bench-scale studies provide qualitative information (what and why). However, field studies provide quantitative information (how much and how long). These time-controlled studies may take months or years to provide data to advance the technology to large-scale site trials.

3) There is a lack of emerging technologies to treat inorganic contaminants.

All of the treatment technologies reviewed are designed to treat organic contaminants and only two recovery technologies are specifically designed toward solubilizing or mobilizing inorganic compounds. However, approximately 20% of Superfund sites have ground-water contaminated by lead, arsenic or chromium. Therefore, only two technologies are being developed to address hundreds of sites contaminated with inorganics.

4) The development of delivery systems is as important as the development of the technology.

Techniques to deliver *in situ* treatments to contaminated ground water are complicated and underdeveloped. While some researchers are developing technologies along with the necessary delivery systems, others are relying on existing delivery systems such as well injection or trench infiltration. Incompatibility between technology and delivery systems can cause technical problems that decrease efficiency. Consequently, the success of a technology is partially contingent on its compatibility with the delivery system.

RECOMMENDATIONS

1) **All major stakeholders should take a lead in improving the development and diversity of ground-water remediation technologies. Information-sharing among all parties needs to be improved as well.**

   All stakeholders involved in ground-water remediation would benefit if more technologies were available. Site conditions and contaminant characteristics are unique. Consequently, a standardized cleanup technology (pump-and-treat) cannot meet all the requirements for efficient remediation. For example, the technologies required to clean up an aquifer contaminated with TCE in a fractured rock matrix are not the same as those to clean up an aquifer contaminated with hexavalent chromium in a coarse sand matrix. A variety of treatment technologies and delivery systems are needed to accommodate the complexities of each site. The few technologies now being developed cannot effectively meet the needs of the tens of thousands of ground-water remediation projects in the CERCLA, RCRA and UST programs. EPA, DOE, and DOD, as well as other stakeholders, should take a lead in improving the development, diversity, and information-sharing of ground-water remediation technologies.

2) **Stakeholders involved in ground-water remediation should be convened to exchange ideas and experiences for improving the state of technology.**

   Activities and opinions from the private sector may not have been adequately defined during this survey. Most of the information was obtained from scientists and databases either partially or wholly supported by the government. However, there may be advances developed by research supported by private industry. A continuing forum of industry representatives, government and private researchers, regulators, consultants and contractors who are involved in ground-water remediation should be held. The purpose would be to discuss successes and failures, barriers to using more efficient ground-water remediation methods and courses of action which could be taken to increase the diversity of available technologies.

3) **Information and data from field demonstrations and applications should be stored and managed in an accessible manner.**

   Specifically, the location of and contact person for each project, as well as a brief description of the technology used, should be easily accessible. Some of this information is already captured in the RODS database and the Bioremediation Field Initiative databases, but additional information could be obtained from the Underground Storage Tank (UST) Program, RCRA corrective action sites and other remediation projects regulated by the states. Improving communication between technology practitioners and users will decrease the risk of making uninformed decisions.

4) **The adequacy of delivery systems for *in situ* technologies should be examined.**

   Some researchers are developing delivery systems concurrent with a technology. We suspect, however, that many systems are being planned and constructed in the field without benefit

of the normal developmental phases. Documentation of this trial-and-error process may help other users apply the technology more efficiently.

5) **Demonstration projects could be directed more towards *in situ* ground-water treatment.**

In the SITE program, there are two *in situ* ground-water technologies in the 78 proposed or existing demonstrations and four *in situ* ground-water technologies in the 44 emerging technologies. Ground-water contamination is found at approximately 75% of NPL sites. Clearly, the percentage of projects directed at the problem is disproportionately low. Other Federal agencies should evaluate the activities in their demonstration programs to further support *in situ* ground-water technologies.

BIBLIOGRAPHY

Publications

1. An Open File Report, 90-139, United States Geological Service Water Resources Research Grant Program, Reston, VA, 1990.

2. H. Beller, E. Edwards, D. Grbic-Galic, et al., Microbial Degradation of Alkylbenzenes under Sulfate-Reducing and Methanogenic Conditions, EPA/600/S2-91/027, United States Environmental Protection Agency, Cincinnati, 1991.

3. Bioremediation In the Field, EPA/540/2-90/004, United States Environmental Protection Agency, Cincinnati, 1990.

4. Bioremediation In the Field, EPA/540/2-91/007, EPA/540/2-91/018 and EPA/540/2-91/027, United States Environmental Protection Agency, Cincinnati, 1991.

5. Forum on Innovative Hazardous Waste Treatment Technologies, Domestic and International, EPA/540/2-89/005, United States Environmental Protection Agency, Cincinnati, 1989.

6. Hazardous Substance Research Centers Program, Program Summary FY 1991, 21R-1005, United States Environmental Protection Agency, Washington, 1991.

7. J. Keely, Performance of Pump-and-Treat Remediation, EPA/540/4-89/005, United States Environmental Protection Agency, Cincinnati, 1989.

8. J. Mercer, D. Skipp and D. Giffin, Basics of Pump-and-Treat Ground-Water Remediation Technology, EPA/600/8-90/003, United States Environmental Protection Agency, Cincinnati, 1990.

9. Second Forum on Innovative Treatment Technologies, Domestic and International, EPA/540/2-90/010, United States Environmental Protection Agency, Cincinnati, 1990.

10. Superfund 90: Proceedings of the 11th National Conference, Hazardous Materials Control Research Institute, Silver Spring, MD, 1990.

11. The Superfund Innovative Technology Program: Technology Profiles, EPA/540/5-90/006, United States Environmental Protection Agency, Cincinnati, 1990.

12. Technology '90, DOE/ER-0484PDE91005072, United States Department of Energy, Washington, 1990.

13. Third Forum on Innovative Hazardous Waste Technologies, Domestic and International, EPA/540/2-91/016, United States Environmental Protection Agency, Cincinnati, 1991.

Papers and Presentations

1. Y. Acar, "Electrokinetic Soil Processing", ASCE Specialty Conference, Ground Improvement and Grouting, New Orleans 1992.

2. A. Abdul et al., Selection of Surfactants for the Removal of Petroleum Products from Shallow Sandy Aquifers. Ground Water 28(6), 1990.

3. N. Baek and P. Jaffe, The Degradation of Trichloroethylene in Mixed Methanogenic Cultures, J. Env. Qual., 18(4), 1988.

4. R. Brown and R. Fraxadas, Air Sparging - Extending Volatilization to Contaminated Aquifers, Groundwater Technologies, Inc., Trenton, NJ, unpublished paper, 1991.

5. C.T. Chiou et al., Water Solubility Enhancement of Some Organic Pollutants and Particles by Dissolved Humic and Fulvic Acids., Environ. Sci. Technol., Vol. 20, No. 5, 1986.

6. J. Fu and R. Luthy, Aromatic Compound Solubility in Solvent/Water Mixtures, Journal of Environmental Engineering, Vol. 112, No. 2, April 1986.

7. B. Herrling et al., "UVB Technique for In Situ Groundwater Remediation of Strippable Contaminants: Operation and Dimensioning of Wells," in Proceedings of Hazardous Waste Management, Contaminated Sites and Industrial Risk Assessment, International Society for Environmental Protection, Vienna, Austria, 1990.

8. D. Mackay and J. Cherry, Groundwater Contamination: Pump-and-Treat Remediation, Env. Sci. and Tech., 23(6), 1989.

9. R. Rao et al., Sorption and Transport of Hydrophobic Organic Chemicals in Aqueous and Mixed Solvent Systems: Model Development and Preliminary Evaluation, Journal Environ. Qual., Vol. 14, No. 3, 1985.

10. J. Shuring and P. Chan, "Application of Pneumatic Fracturing to Remove Contaminants from the Vadose Zone," in Proceedings of the Water Quality Management of Landfills, Water Pollution Control Federation, Chicago, 1990.

11. J. Shuring and P. Chan, "Simulation of Contaminant Removal in the Vadose Zone by Pneumatic Fracturing", in Proceedings of the Canadian Congress on Applied Mechanics, Canadian Congress on Applied Mechanics, Winnipeg, 1991.

12. J. Thomas and H. Ward, In Situ Biorestoration of Organic Contaminants in the Subsurface, Env. Sci. and Tech., 23(7), 1989.

13. B. Vignon and A. Rubin, Practical Considerations in the Surfactant-aided Mobilization of Contaminants in Aquifers., J. Water Pollution Control Federation, 61(7), 1989.