In Situ Remediation Technology Status Report:

Cosolvents

U.S. Environmental Protection Agency Office of Solid Waste and Emergency Response Technology Innovation Office Washington, DC 20460

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Notice

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Foreword

The purpose of this document is to describe recent field demonstrations, commercial applications, and research on technologies that either treat soil and ground water in place or increase the solubility and mobility of contaminants to improve their removal by pump-and-treat remediation. It is hoped that this information will allow more regular consideration of new, less costly, and more effective technologies to address the problems associated with hazardous waste sites and petroleum contamination.

This document is one in a series of reports on demonstrations and applications of in situ treatment technologies. To order other documents in the series, contact the National Center for Environmental Publications and Information at (513) 489-8190 or fax your request to NCEPI at (513) 489-8695. Refer to the document numbers below when ordering.

EPA542-K-94-003Surfactant EnhancementsEPA542-K-94-004Treatment WallsEPA542-K-94-005Hydrofracturing/Pneumatic FracturingEPA542-K-94-006CosolventsEPA542-K-94-007ElectrokineticsEPA542-K-94-009Thermal Enhancements

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Abbreviations

BTEX	=	Benzene, Ethylbenzene, Toluene, Xylene
CERCLA	=	Comprehensive Environmental Response, Compensation, and Liability Act

- DNAPL = Dense Non-Aqueous Phase Liquid
- DOE = Department of Energy
- PAH = Poly-Aromatic Hydrocarbons
- PCE = Tetrachloroethylene
- RCRA = Resource Conservation and Recovery Act
- SITE = Superfund Innovative Technology Evaluation Program
- SVE = Soil Vapor Extraction
- SVOC = Semi-Volatile Organic Compound
- TCA = 1,1,1-Trichloroethane
- TCE = Trichloroethylene
- TPH = Total Petroleum Hydrocarbon
- VOC = Volatile Organic Compound

Purpose and Process

This document describes the development and application of in situ solvent enhancement as a technology to remove contaminants from soils and ground water at waste disposal and spill sites. The activities described include research, demonstrations, and field applications of the technology.

Information in this report was obtained from computerized databases such as the Dialog Information Services, the Environmental Protection Agency's (EPA) Vendor Information System for Innovative Treatment Technologies (VISITT), and EPA's Alternative Treatment Technologies Information Center (ATTIC). Information also came from publications such as EPA's Superfund Innovative Technology Evaluation (SITE) Profiles and the Department of Energy's (DOE) Office of Technology Development Program Reports. This information was supplemented with telephone interviews with representatives of federal agencies, academic research centers, and hazardous waste remediation consulting firms. In some cases, the data concerning the performance of the technology were provided by the technology vendor.

Technology Needs

Treatment of aquifers contaminated by non-aqueous phase liquids (NAPLs) by traditional pump-and-treat systems has proven impracticable. NAPLs have very low solubility in water and tend to exist as pockets at the subsurface location to which they have migrated. They dissolve slowly, leading to very slow rates of removal by pumping. To improve this performance, new technologies are being developed to mobilize or solubilize these pockets.

Environmental professionals are acknowledging the limitations of pump-and-treat techniques to clean ground water contaminated with organic solvents. Excavation of contaminated soil is another option. However, this can be very expensive if a large volume of soil is affected because the soil still needs to be treated.

Technology Description

In situ solvent flushing involves injecting a solvent mixture (e.g., water plus a miscible organic solvent such as alcohol) into either the vadose zone, the saturated zone, or both to extract organic contaminants. Cosolvent flushing can be applied to soils or ground water to solubilize either the source of contamination or the contaminant plume emanating from it. The cosolvent mixture is injected upgradient of the contaminated area. The solvent with the dissolved contaminants is extracted downgradient and treated above ground. Physical barriers may be installed to prevent uncontrolled migration of solvent and contaminants.

Cosolvents can promote contaminant removal in two ways. The first is by increasing the apparent solubility of the contaminant in water, which improves the mass removal per pore volume. The second is by reducing interfacial tension between the water and the contaminant, which may result in direct mobilization of NAPLs. Cosolvents that microbes can use as substrates may have the added advantage of promoting bioremediation if they are used at nontoxic levels.

Researchers also are exploring the effect of the inclusion of cosolvents in other types of remediation. A methanol/water cosolvent has been shown to improve the supercritical CO_2 extraction of DDT from soil and cosolvents added to potassium permanganate (KMnO₄) improved the degradation (by oxidation) of the common dense non-aqueous-phase liquids trichloroethylene and perchloroethylene.

Hill Air Force Base, Utah University of Florida and R.S. Kerr Environmental Research Laboratory

Description of Demonstration: EPA is funding, through a cooperative agreement with the University of Florida, a field test of in situ solvent extraction at Hill AFB in Utah.

The water table at the site has declined in the past few years due to drought conditions, so researchers will raise the water table to the top of the contaminant zone before injecting an ethanol/water mixture into the gravelly sand in a 3 meter by 5 meter test cell to solubilize the light non-aqueous phase liquid (LNAPL).

Contamination in the test bed is predominantly jet fuel with some pesticides and chlorinated solvents mixed in. There were multiple sources of contamination: fire training site and chemical waste pits. The LNAPL mixture occurs as a coating on particles and as globules in pore spaces in the ground water and above it in the vadose zone.

Wastes Treated: BTEX (jet fuel), pesticides, VOCs, SVOCs

Status: Initial site characterization has been completed. Researchers will begin injecting the cosolvent mixture in March 1995. The injection and extraction process will last for one month. A report of the findings is scheduled for late 1995.

Preliminary Results: None yet.

Future work at this site

A project to study the use of solvents to promote mobilization of residual organic phase was recently funded as was a comparative study on the effectiveness of cosolvents, surfactants, air and steam to extract contaminants at this site.

Future work at another site

At a site not yet selected, researchers will evaluate cosolvent-enhanced mobilization and solubilization under different hydrogeological conditions and for different waste mixtures.

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References:

Augustijin, D.C.M. and Rao, P.S.C. "Enhanced Removal of Organic Contaminants by Solvent Flushing." ACS Symposium Series (submitted), 1995.

Augustijin, D.C.M.; Dai, D.; Rao, P.S.C.; and Wood, A.L. "Solvent Flushing Dynamics in Contaminated Soils." In *Transport and Reactive Processes in Aquifers*. T.H. Dracos and F. Stouffer (eds.). Balkema/Rotterdam/Brookefield, 1994.

Augustijin, D.C.M.; Jessup, R.E.; Rao, P.S.; and Wood, A.L. "Remediation of Contaminated Soils by Solvent Flushing". *Journal of Environmental Engineering*, 120 (1) Jan/Feb 1994, p 42-57.

Rao, P.S.C.; Lee, L.S.; and Wood, A.L. Solubility, Sorption, and Transport of Hydrophobic Organic Chemicals in Complex Mixtures. U.S. Environmental Protection Agency, EPA/600-M-91-009, March 1991.

Wood, A. Lynn; Bouchard, D; Brusseau, M.; and Rao, P.S.C. "Cosolvent Effects on Sorption and Mobility of Organic Contaminants in Soils." *Chemosphere*, 21 (4-5) 1990, p 575-587.

Removal of Gasoline from Sandy Aquifer Material Rice University

Description of Research: Researchers studied the use of cosolvents and surfactants for the removal of residual aviation fuel from aquifer material from a U.S. Coast Guard base in Traverse City, Michigan.

Alcohols at 20% concentration did not mobilize the contaminants from the soil column. 2-Propanol mobilized the contaminant at 50% concentration while 50% methanol showed little effect.

Wastes Treated: BTEX

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Reference:

Kan, A.T.; Tomson, M.B.; McRae, T.A. "Enhanced Mobilization of Residual Aviation Gasoline in Sandy Aquifer Material by Surfactant and Cosolvent Flush," *Proceedings of the 203rd American Chemical Society National Meeting*, San Francisco, California, April 1992.

Boyd, G.R. and Farley, K.J. "NAPL Removal from Groundwater by Alcohol Flooding: Laboratory Studies and Applications." In *Hydrocarbon Contaminated Soils and Groundwaters: Analysis, Fate, Environmental and Public Health Effects, and Remediation*. P. Kostecki, E. Calabrese, and C. Bell (eds.). Ann Arbor, MI: Lewis Publishers, 1992.

Brandes, D. and Farley, K.J. "Importance of Phase Behavior in Remediation of Dense Nonaqueous Phase Liquid (DNAPL) Contaminated Aquifers by Alcohol Flooding." *Proceedings of Spectrum '92, Nuclear and Hazardous Waste Management, International Topical Meeting*, Boise, Idaho, 1992.

Broholm, K. and Cherry, J.A. "Enhanced Dissolution of Heterogeneously Distributed Solvents Residuals by Methanol Flushing—A Field Experiment." *Transport and Reactive Processes in Aquifers*. Draces and Stouffer (eds.), Balkema/Rotterdam/Brookefield, 1994.

Brusseau, M.L. *Complex Mixtures and Groundwater Quality*. U.S. Environmental Protection Agency, EPA/600/S-93/004, September 1993.

Dooley, K.M.; Ghonasgi, D.; Knopf, F.G.; Gambrell, R.P. "Supercritical CO₂-Cosolvent Extraction of Contaminated Soils and Sediments." *Environmental Progress*. 9 (4) 1990, p 197.

Farley, J.A. "Technical Feasibility and Conceptual Design for Using Supercritical Fluid to Extract Pesticides from Aged Soil." *Remediation*. 4 (3) 1994, p 301.

Palmer, C.D. and Fish, W. *Chemical Enhancements to Pump-and-Treat Remediation*. U.S. Environmental Protection Agency, EPA/540/S-92/001, September 1992.

Rixey, W.G.; Johnson, P.C.; Deeley, G.M.; Byers, D.L.; and Dortech, I.J. "Mechanisms for the Removal of Residual Hydrocarbons from Soils by Water, Solvent, and Surfactant Flushing." In *Hydrocarbon Contaminated Soils and Groundwater: Analysis, Fate, Environmental and Public Health Effects, and Remediation.* P. Kostecki, E. Calabrese, and C. Bell (eds.). Ann Arbor, MI: Lewis Publishers, 1992.