

EPA542-K-94-004
April 1995

In Situ Remediation Technology Status Report:

Treatment Walls

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

Acknowledgements

The authors would like to thank all the researchers and technology developers described in this report for their assistance in its preparation. We especially would like to thank Steve McCutcheon at the U.S. EPA Environmental Research Laboratory in Athens, Georgia; Robert Puls at the U.S. EPA Robert S. Kerr Environmental Research Laboratory in Ada, Oklahoma; and Stephen Shoemaker at DuPont Engineering for reviewing the draft document and making valuable suggestions for improvement.

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Notice

This material has been funded by the United States Environmental Protection Agency under contract number 68-W2-0004. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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.

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Abbreviations

BTEX	= Benzene, Toluene, Ethylbenzene, Xylene
CERCLA	= Comprehensive Environmental Response, Compensation, and Liability Act
DCE	= Dichloroethene
DNAPL	= Dense Non-Aqueous Phase Liquid
DOE	= Department of Energy
PAH	= Poly-Aromatic Hydrocarbon
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

Introduction

Purpose and Process

The purpose of this document is to describe demonstrations, field applications, and research on treatment walls for remediating contaminated ground water at waste disposal and spill sites.

Information for this report came from computerized databases such as the Dialog Information Services and the Environmental Protection Agency's (EPA) Vendor Information System for Innovative Treatment Technologies (VISITT) and Alternative Treatment Technologies Information Center (ATTIC). Additional materials were obtained from publications such as the Hazardous Substance Research Center Annual Reports, Superfund Innovative Technology Evaluation Technology Profiles and Department of Energy's Office of Technology Development Program Summary as well as conference summaries, proceedings and compendiums. Personal interviews and discussions with representatives of other federal agencies, academic research centers, and hazardous waste remediation consulting firms provided supplementary information.

Technology Needs

Numerous hazardous waste sites have significant concentrations of metals, halogenated organic compounds, and radionuclides that contaminate ground water. Traditional technologies, such as pump and treat, require an external energy source and their cost is high. Subsurface residuals frequently remain at undesirable levels. Thus, subsurface permeable treatment walls are being considered as a cost-effective in situ water treatment alternative.

Technology Descriptions

Water permeable treatment walls are installed as permanent, semi-permanent, or replaceable units across the flow path of a contaminant plume, allowing the plume to move passively through while precipitating, sorbing, or degrading the contaminants. These mechanically simple barriers may contain metal-based catalysts for degrading volatile organics, chelators for immobilizing metals, nutrients and oxygen for microorganisms to enhance bioremediation, or other agents. Degradation reactions break down the contaminants in the plume into harmless byproducts. Precipitation barriers react with contaminants to form insoluble products that are left in the barrier as water continues to flow through. Sorption barriers adsorb or chelate contaminants to the barrier surface. The reactions that take place in barriers are dependent on parameters such as pH, oxidation/reduction potential, concentrations, and kinetics. Thus, successful application of the technology requires characterization of the contaminant, ground-water flux, and subsurface geology. Although most barriers are designed to operate in situ for years with minimal maintenance and without an external energy source, the stability of aging barriers has not been established.

The following pages contain descriptions of completed, ongoing, and future demonstrations and commercial applications as well as current research and testing of passive treatment walls.

Completed Demonstrations

Canadian Forces Base Borden, Ontario, Canada Waterloo Centre for Groundwater Research, University of Waterloo In Situ Permeable Reaction Wall

Description of Demonstration: Researchers installed a permeable reaction wall containing an iron-based catalyst about 16.5 feet downgradient from the source of a contaminant plume to pilot test the capability of the wall to degrade halogenated organic compounds. The plume was about 6.5 feet wide and 3.3 feet thick with maximum concentrations along the axis of about 250,000 $\mu\text{g/L}$ trichloroethene (TCE) and 43,000 $\mu\text{g/L}$ tetrachloroethene (PCE). The source of the plume was located about 13 feet below ground surface and 3.3 feet below the water table. (Investigators believe the wall can be installed to depths of 50 feet, but no test results are available at this time to substantiate this.)

Using sealable joint sheet piling, a rectangular cell was constructed on the surface and driven to a depth of 32 feet, the cell was sealed and dewatered and the native sand was replaced by the reactive material consisting of 22% by weight granular iron and 78% by weight coarse sand. The sand, which was coarser than the native materials, ensured that the wall would be more permeable than the surrounding sand. After installing the reactive material, the sheet piling was completely removed and natural flow conditions were achieved. The wall dimensions were 18 feet long, 5.2 feet thick, and 7.2 feet deep and it was positioned 3.3 feet below the water table.

Wastes Treated: VOCs

Status: The pilot test was completed in 1993. The Waterloo Centre for Groundwater Research is part of Ontario's Centres of Excellence program, a government sponsored partnership with academia and industry.

Demonstration Results: Multilevel monitoring wells were located 1.6 feet upgradient of the wall, in the wall at distances of 1.6 and 3.3 feet, and 1.6 feet downgradient of the wall for a total of 348 sampling points. Concentration distributions through the wall were determined on 13 occasions over 474 days, during which there was no decline in the effectiveness of the barrier. Most of the mass loss occurred within the first 50 cm of the wall; at greater distances into the wall, performance was below that expected. However, the reaction wall reduced the TCE concentration by 95% and the PCE concentration by 91%. No vinyl chloride was detected in the samples. Increased chloride concentrations downstream of the wall were consistent with the quantity of TCE and PCE that had been degraded. Only trace amounts of dichloroethene (DCE) were detected downstream of the wall.

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References:

O'Hannesin, S.F. *A Field Demonstration of a Permeable Reaction Wall for the In Situ Abiotic Degradation of Halogenated Aliphatic Organic Compounds*. Master's Thesis, University of Waterloo, Waterloo, Ontario, Canada. 1993.

O'Hannesin, S.F. and Gillham, R.W. "A Permeable Reaction Wall for In Situ Degradation of Halogenated Organic Compounds." 45th Canadian Geotechnical Society Conference, Toronto, Ontario, October 25-28, 1992.

O'Hannesin, S.F. and Gillham, R.W. "In Situ Degradation of Halogenated Organics by Permeable Reaction Wall." *Ground Water Currents*, March 1993, EPA/542/N-93/003.

Borden Aquifer, Ontario, Canada
Waterloo Centre for Groundwater Research, University of Waterloo
In Situ Permeable Reaction Wall

Description of Demonstration: Researchers field tested a proprietary solid peroxide formulation (an oxygen-releasing compound) to determine whether it could provide dissolved oxygen in a controlled steady manner to enhance biodegradation of BTEX-contaminated ground water. Benzene and toluene were injected into ground water to represent BTEX compounds, and their fate was monitored over several weeks along four lines of monitoring wells.

Wastes Treated: BTEX

Status: Completed.

Demonstration Results: The results indicate that the oxygen releasing compound can support biodegradation of benzene and toluene at concentrations typical of those found at petroleum contaminated sites.

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References:

Bianchi-Mosquera, G.C.; Allen-King, R.M.; and Mackay, D.M. "Enhanced Degradation of Dissolved Benzene and Toluene Using a Solid Oxygen-Releasing Compound" *Ground Water Monitoring and Remediation*, Winter 1994, p 120-128.

Ongoing and Future Demonstrations

Canadian Forces Base Borden Waterloo Centre for Groundwater Research, University of Waterloo In Situ Permeable Reaction Wall

Description of Demonstration: Researchers are field testing an in situ semipassive permeable wall into which nutrient solutions that enhance biodegradation of organics are introduced. The wall is installed across the path of a contaminant plume in an unconsolidated aquifer.

Wastes Treated: TCE, carbon tetrachloride

Status: Ongoing

Demonstration Results: Results indicate that by adding substances in the wall, the mixing with ground water is maximized to produce a stable microbial population that can be supported at some distance downgradient from the wall. An anaerobic population supporting this led to complete carbon tetrachloride removal from ground water, but did not transform TCE. Work is continuing to overcome this limitation.

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Reference:

Devlin, J.F. and Barker, J.F. "A Semipassive Nutrient Injection Scheme for Enhanced In Situ Bioremediation." *Ground Water*, 32 (3), 1994, p 374.

General Electric, Sunnyvale, California EnviroMetal Technologies Metal-Enhanced Abiotic In Situ Treatment of VOCs

Description of Demonstration: An above-ground field test reactor containing 50% iron was installed at this semiconductor manufacturing facility to test the feasibility of installing an in situ permeable reactive zone. Ground water was pumped through the reactor at a rate of 4 feet/day for 9 months. Initial concentrations of contaminants were 50-200 ppb trichloroethene (TCE), 450-1000 ppb cis-1,2-dichloroethene (cis-DCE), 100-500 ppb vinyl chloride (VC), and 20-60 ppb Freon-113. The time required to degrade one-half of the contaminant mass in the above-ground field test was <1.7 hours for TCE, 1-4 hours for cis-DCE, 2-4 hours for VC, and <1.6 hours for Freon-113. Mineral precipitation, hydrogen gas production, and microbial effects also were evaluated.

Wastes Treated: TCE, DCE, vinyl chloride, Freon-113

Status: Based on the feasibility tests described above, a full-scale in situ permeable treatment wall was approved by the state regulatory agency and was installed in December 1994. The permeable reactive

zone, which will be 4 feet thick, 40 feet long, 10 feet high, and about 25-30 feet deep, will contain 100% reactive iron. It will be installed using a trench box design. The estimated cost is projected to be \$175,000-\$200,000. Patents governing the in situ application of the metal enhanced dehalogenation are held by the University of Waterloo. EnviroMetal Technologies, Inc. holds an exclusive license with the University of Waterloo for this treatment technology.

Demonstration Results: None yet

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Reference:

Gillham, R.W. and O'Hannesin, S.F. "Metal Catalyzed Abiotic Degradation of Halogenated Organic Compounds." *Ground Water*, 29 (5), 1991, p 752.

**Industrial Facility, New York State
EnviroMetal Technologies and Waterloo Groundwater Control Technologies
Metal-Enhanced Abiotic In Situ Treatment of VOCs
Using Funnel-and-Gate™ System**

Description of Demonstration: VOCs will be degraded using the EnviroMetal process (metal-enhanced reductive dehalogenation) in a pilot-scale Funnel-and-Gate™ in situ treatment system at a former plating facility contaminated with chlorinated solvents. The reactive zone, containing 100% granular iron, will be 10 feet wide, 3 feet thick, and installed at a depth of 15 feet, which is below the water table and near the source of the contaminant plume. Ground water will be directed towards the zone by 15 linear feet of Waterloo Barrier sheetpiling on either side. There is a confining layer of clay at 15 feet.

Wastes Treated: VOCs and SVOCs, including TCE, PCE, DCE, and vinyl chloride

Status: A pilot-scale unit was installed in May 1995. After the system is operating, the demonstration is expected to run for 6 months. The New York State Department of Environmental Conservation and U.S. EPA's SITE program are overseeing the demonstration. EnviroMetal Technologies Inc. holds an exclusive license with the University of Waterloo, the patent holder, for the commercial application of this treatment technology. Waterloo Groundwater Control Technologies, Inc. is commercializing the Funnel-and-Gate™ system (patents pending) developed at the Waterloo Centre for Groundwater Research.

Demonstration Results: None yet

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Gillham, R.W. and O'Hannesin, S.F. "Metal Catalyzed Abiotic Degradation of Halogenated Organic Compounds." *Ground Water*, 29 (5), 1991, p 752.

**Semiconductor Manufacturing Facility, New Jersey
EnviroMetal Technologies
Metal-Enhanced Abiotic In Situ Treatment of VOCs**

Description of Demonstration: Batch and column tests using 50% and 100% iron in the reactive media and ground water flowing at 1.5 feet/day were conducted to establish reaction conditions for a pilot-scale above-ground field trial (now underway). These tests are for the future installation of an in situ treatment wall.

Wastes Treated: TCE, PCE, DCE, vinyl chloride

Status: An above-ground field trial began in November 1994 under the EPA SITE demonstration program and is still operating. The field trial results should be published by the end of 1995.

Additional sites where feasibility studies have been completed or are underway include:

- Twin Cities Army Ammunition Plant in St. Paul, Minnesota (sponsored by the Minnesota Pollution Control Agency) to treat TCE, PCE, and cis-1,2-dichloroethene
- Closed landfill in New Mexico
- Industrial facilities in Massachusetts, California, and New York
- Air Force facilities in Utah and Washington State (large-scale field tests scheduled to occur in 1995 at Hill AFB, Utah, will involve the use of a funnel-and-gate system with the iron filings to treat TCE)

Demonstration Results: Results are not yet available. The column test results showed half-life degradation rates of 0.7 hours for PCE (4000 to 12000 ppb initially) at 50% iron and 0.4 hours at 100% iron; and for TCE (400 to 1000 ppb initially) 1.1 hours at 50% iron and 0.5 hours at 100% iron.

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Reference:

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**AFB/Massachusetts Military Reserve, Falmouth, Massachusetts
Waterloo Centre for Groundwater Research, University of Waterloo
Metal-Enhanced Abiotic Treatment of VOCs Using a Funnel-and-Gate™**

Description of Demonstration: A pilot-scale test using granular iron in a Funnel-and-Gate™ system is planned to treat a large and deep contaminant plume containing VOCs. The system will be installed near the leading edge of the plume, which is 40 to 100 feet thick and 180 feet deep.

Wastes Treated: VOCs

Status: A preliminary test was conducted in the spring of 1995.

Demonstration Results: The test failed to reach the 180 foot depth. Consequently, the reaction zone and Funnel-and-Gate™ system will not be pilot tested on that deep plume. Other options for the deep plume are under consideration by the National Guard, who is sponsoring the demonstration. The reaction zone and Funnel-and-Gate™ system may be tested on two other, more shallow, plumes at the site.

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Gillham, R.W. and O'Hannesin, S.F. "Metal Catalyzed Abiotic Degradation of Halogenated Organic Compounds." *Ground Water*, 29 (5), 1991, p 752.

**Hanford 100D Area, Washington
Battelle Pacific Northwest Laboratories
In Situ Redox Manipulation Project**

Description of Demonstration: Field experiments are planned for the Arid Soils VOC Integrated Demonstration to test the feasibility of in situ redox manipulations with chemical reagents using a forced gradient, single well, reactive tracer test. Field experiments will involve injecting the reagent sodium dithionite into the aquifer creating a 60 to 100 foot diameter geochemical barrier in advance of a contaminant plume. After allowing 5 to 30 days for the reaction to occur, water containing the reaction byproducts and any remaining reagent will be pumped out. The longevity of the system to maintain a reducing environment also will be evaluated.

Wastes Treated: Chromium

Status: The demonstration is scheduled for summer 1995. The researchers have conducted an initial site characterization using existing monitoring wells and have submitted a draft test plan to DOE, EPA, and the State of Washington Department of Ecology. The Department of Energy is sponsoring the research.

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Reference:

Fruchter, J.S. *In Situ Redox Manipulation: Enhancement of Contaminant Destruction and Immobilization*. Semi-Annual Office of Technology Development (OTD) Information Meeting (2nd), Houston, Texas, January 26-28, 1993, NTIS Order Number DE93007877, 7p.

**DOE Savannah River, South Carolina
Barrier Membrane Corporation
Treatment Wall**

Description of Demonstration: Researchers are constructing a gravel trench 300 feet long by 30 feet deep that will intersect the highest contaminant concentration of a contaminant plume. Pumping wells will be constructed within this wall to remove contaminated ground water but the major focus is to study the hydraulics. The studies are designed to investigate ground-water retention time in the wall and problems associated with injecting a treatment medium in the gravel matrix. The contaminant plume is shallow and the surrounding soils are interbedded clays and sands.

Wastes Treated: Chromium, nickel, lead and cadmium

Status: Under construction. Pump tests are scheduled for July and August 1995.

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**Coast Guard Air Station, Elizabeth City, North Carolina
U.S. EPA Environmental Research Laboratory, Ada, OK
Treatment Wall**

Description of Demonstration: A series of large-diameter augered holes in a staggered 3-row array were located within an aquifer to intercept a contaminant plume of chromate and chlorinated organics. A mixture (by volume) of 50% iron filings (two types), 25% clean coarse sand, and 25% aquifer material was poured down hollow-stem augers from 22 feet to 10 feet below ground surface. Each iron column was approximately 8 inches in diameter and a total of twenty-one columns were installed in a 60 square foot area. The mixed waste contaminant plume is between 14 and 20 feet below ground surface and the water table ranges from 5 to 6 feet below ground surface. One iron type was shown to be an effective reductant for chromate in a two-year laboratory study by RSKERL scientists, while the other iron has been shown to be more effective in the reductive dechlorination of the organics. This field experiment is evaluating the effectiveness of this method of treatment wall emplacement and is providing additional in situ field data for full field-scale implementation.

Wastes Treated: TCE, DCE, vinyl chloride, and Cr⁺⁶

Status: The demonstration has been in operation since September 1994.

Preliminary Results: Preliminary results show complete reduction of Cr⁺⁶ to below detection (<0.01 mg/L) limits and greater than 75% reduction in initial TCE concentrations and reduction of vinyl chloride concentrations to less than 1 μ g/L. These results are very promising, especially for the chlorinated organics, because the experiment was primarily designed to optimized chromate remediation, not the chlorinated organics. Longer residence times are planned for the latter in the full field scale test to be installed in August 1995.

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References:

Puls, R.W.; Powell, R.M.; and Paul, C.J. "In Situ Remediation of Ground Water Contaminated with Chromate and Chlorinated Solvents Using Zero-Valent Iron: A Field Study." *Proceedings of the 209th American Chemical Society National Meeting, Anaheim, California, April 2-7, 1995*. 35 (1), p 788-791.

**Several Sites in Canada and the United States
Waterloo Centre for Groundwater Research
In Situ Permeable Reaction Wall for Treatment of Inorganics**

Description of Demonstration: Inorganic contaminants in ground water are treated using in situ porous reactive walls. Wall materials are placed in the path of the plume and react with the contaminant via reduction and precipitation. This technology is being developed for treating mine and industrial wastes, and septic system and agricultural effluent.

Wastes Treated: Inorganics, especially metals, SO₄ and PO₄ radionuclides

Status: Field trials are ongoing to remove dissolved Cr, Fe, SO₄ and PO₄

Results: Preliminary results indicate contaminant concentrations are decreased by orders of magnitude and to below drinking water levels.

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References:

Blowes, D.W. and Ptacek, C.J. "Geochemical Remediation of Groundwater by Permeable Reactive Walls: Removal of Chromate by Reaction with Iron-Bearing Solids." *Proceedings of the Subsurface Restoration Conference, Third International Conference on Groundwater Quality Research, June 21-24, 1992, Dallas, Texas*, p 214-216.

Blowes, D.W. and Ptacek, C.J. System for Treating Contaminated Groundwater (Redox Curtain). United States Patent 5,362,394. 1994.

Blowes, D.W.; Ptacek, C.J.; Bain, J.G.; Waybrant, K.R.; and Robertson, W.D. "Treatment of Mine Drainage Water Using In Situ Permeable Reactive Walls." *Proceedings of the Sudbury 1995 Mining and the Environment Conference, May 28-June 1, 1995, Sudbury, Ontario*.

**Valley Wood Treating, Turlock, California
In Situ Remediation of Chromium in Ground Water
GEOCHEM (A Division of Terra Vac)**

Description of Technology Use: The process removes chromium from contaminated ground water using a variation of traditional pump-and-treat methods. Contaminated ground water is brought to the surface and treated using conventional treatment systems such as ferrous iron. A reductant is added to the treated water which is reinjected around the plume margin where it reacts and reduces residual levels of chromium, forming a precipitate. Such reinjection creates a “barrier” of elevated water levels around the plume, enhancing the gradient and associated hydraulic control. The reinjection also allows for in situ reduction and subsequent fixation of residual chromium.

Wastes Treated: Cr⁺⁶

Status of Demonstration and Development: The technology was accepted into the SITE Program in the summer of 1992. Arrangements are being made to demonstrate the technology in 1995.

Demonstration Results: None yet.

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Current Research

Reaction Mechanisms in Permeable Reactive Barriers ManTech Environmental Research Services Corporation and U.S. EPA Environmental Research Laboratory, Ada, OK

Description of Research: Research during the past three years has evaluated the impact of subsurface geochemistry and mineralogy on chromate reduction by zero-valent metals in permeable reactive barriers. When reduced from Cr(VI) to Cr(III) the chromium becomes less toxic and its mobility is reduced due to precipitation and adsorption, effectively remediating the aquifer. This research had multiple objectives, which were to determine:

- 1) whether corrosion processes, including cathodic reduction, are responsible for the removal of solution CrO_4^{2-} by elemental metals, primarily iron,
- 2) if removal would occur in systems incorporating aquifer materials,
- 3) the rates and mechanisms of the CrO_4^{2-} removal,
- 4) the form and location of the removed chromium,
- 5) how iron type, geochemical, and mineralogical differences affect these reactions and,
- 6) whether this remediation approach is suitable for a CrO_4^{2-} plume at the U.S. Coast Guard Air Support Center, Elizabeth City, North Carolina.

Numerous stirred batch reactor and shaken batch bottle experiments to test chromate reduction have been performed using two different aquifer sediments and a silica sand, seven types of iron, titanium, magnesium, aluminum, various metal pretreatments and seven aluminosilicate minerals. Aluminosilicate dissolution in these systems has also been evaluated. Chromate adsorption and desorption studies as well as electron probe microscopic analyses of the reacted materials have been carried out.

The results have shown that CrO_4^{2-} in solution can be reduced to Cr(III) by corrosion mechanisms in the presence of elemental iron. The rate and completeness of chromate reduction are dependent on a complex interaction between metal type, mass, surface area, pretreatment, and aquifer material mineralogy. Exploratory data analysis was performed across several variables for one iron and aquifer material system that reduced chromate rapidly. The resulting multiple regression model showed that 94% of the variation in the chromate reduction half-life was explained by the iron mass and solid:solution ratio.

These corrosion reactions can only proceed when suitable e^- acceptors, such as protons, are present to form an appropriate couple and prevent the accumulation of electric charge. An electrical double-layer model analogue for the metal filing surface has been proposed to explain the reactions that occur. Some types of iron, particularly impure and partially corroded forms, are far more reactive than others for reducing CrO_4^{2-} . Certain aquifer materials contribute more significantly to these reactions due to their mineralogy. Aluminosilicates appear able to provide e^- accepting protons through dissolution, maintaining the corrosion process. A cycle can develop in which rust formation through corrosion promotes additional aluminosilicate dissolution.

Research is continuing on these topics for chromium, along with the potential for enhancing the remediation of other metals using permeable reactive barriers.

Wastes Treated: Chromium

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References:

Powell, R.M. *Geochemical Effects on Chromate Reduction and Remediation Utilizing the Thermodynamic Instability of Zero-Valence-State Iron*. Master's Thesis. University of Oklahoma, Norman, Oklahoma 1994.

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Powell, R.M.; Puls, R.W.; Hightower, S.K.; Sabatini, D.A. "Coupled Iron Corrosion and Chromate Reduction: Mechanisms for Subsurface Remediation." In press for the August 1995 *Environmental Science and Technology*.

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Powell, R.M.; Puls, R.W.; Paul, C.J. "Chromate Reduction and Remediation Utilizing the Thermodynamic Instability of Zero-Valence-State Iron." Water Environment Federation Specialty Conference Series *Innovative Solutions for Contaminated Site Management*. March 6-9, 1994, Miami, Florida.

Powell, R.M. and Puls, R.W. "Abiotic Reduction of Chromate from Zero-Valent Iron Dissolution: Reaction Rates and the Effects of Aquifer Materials." Metal Speciation and Contamination of Aquatic Sediments Workshop, Jekyll Island, Georgia, 1993.

**In Situ Process Based on Zero-Valent Iron
U.S. EPA, Environmental Research Laboratory, Athens, GA**

Description of Research: Stainless steel columns have been designed to address a number of unresolved issues in applying reactive iron treatment walls. These columns provide a greater level of experimental control than those typically being used in reactive iron pilot studies. The columns are designed to measure pH and treatment efficiencies along the length of the column to understand why iron treatment walls lose effectiveness after movement through 10 to 50 cm of media. Innovative iron mixtures are being tested to

overcome pH problems and the inability to achieve drinking water standards and other MCLs. Long-term stability testing is underway (3 to 6 months). Contaminated water from the DOE Savannah River Plant TNX facility will be used for testing in concert with feasibility testing at the University of Waterloo. Data from Waterloo/EnviroMetal pilot tests at Hill AFB have been reviewed, especially those tests where trace amounts of vinyl chloride were observed. These data and results from column studies are being used to develop preliminary guidance on the design and application of funnel-and-gate systems, and other reactive wall configurations. Other efforts focus on the kinetics of the reaction.

Experiments are currently underway to identify and estimate the parameters that control the dechlorination rate of trichloroethene and similar volatile organic compounds in flowing systems exposed to zero-valent iron. These studies examine the effects of mass transfer on the observed conversion rates for various flow velocities, pH, and contaminant concentrations. A rigorous description of the dependence of the conversion rate on the system operating conditions facilitates the development and implementation of this technology. Such detailed knowledge of the physical and chemical factors that control the degradation of ground-water contaminants by granular iron will lead to improved designs of in situ treatment processes.

Potentiostatic and potentiodynamic electrochemical approaches are planned to investigate surface coverage, sorbed species, effects of hydrogen formation, and the elementary rate determining step.

Wastes Treated: TCE, PCE, other chlorinated solvents

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References:

Holser, R.A.; McCutcheon, S.C.; Wolfe, N.L. "The Application of a Rate Expression for the Reductive Dehalogenation of TCE-Contaminated Groundwater to the Design and Performance of a Funnel and Gate System." *Federal Environmental Restoration IV and Defense Cleanup Southeast, Atlanta, Georgia, March 14-15, 1995.*

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**Reduction of Halogenated Hydrocarbons by Metallic Iron
U.S. EPA, Environmental Research Laboratory, Athens, GA**

Description of Research: Kinetic studies have been conducted on the redox reactions of the common ground-water contaminants, tetrachloroethene and trichloroethene in an effort to delineate the reaction mechanism and to identify the degradation products. The dependence of the reaction rate on factors such

as temperature, pH, iron surface area, oxygen concentration, and competing species has been investigated. The focus of the work is to accurately predict the fate of these chlorinated pollutants and to investigate new remediation methods. New reactive iron mixtures have been derived. This study was the first to obtain a rigorous mass balance and pathway analysis of the reductive iron process. Firm hypotheses have been obtained for the nature of the sorption reaction and dechlorination process. Some of the work has been done in collaboration with David Burris of the Air Force Armstrong Laboratory located at Tyndall Air Force Base, Florida.

Wastes Treated: PCE, TCE, other chlorinated solvents

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References:

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Wolfe, N.L.; Peijnenburg, W.; d Hollander, H.; Verboom, H.; v d Meent, D. submitted for publication "Kinetics of Reductive Transformations of Halogenated Hydrocarbons Under Anoxic Reaction Conditions." *Environmental Toxicology and Chemistry*, 1994.

Dechlorination of Pesticides
U.S. EPA, Environmental Research Laboratory, Athens, GA

Description of Research: The degradation of chlorinated pesticides by anaerobic bacteria and separately by zero-valent metals is being studied. Sediment samples have been collected and compared to known contaminated sediments to identify environmental factors that are responsible for anaerobic degradation. These studies have focused on the combination of extraction and reaction to release the bound contaminant from the soil matrix and degrade the solubilized compound. They are also designed to improve analytical methods.

Wastes Treated: Toxaphene, chlordane, DDT and dieldrin

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In Situ Redox Barriers Battelle Pacific Northwest Laboratories

Description of Research: Researchers at Battelle Pacific Northwest Laboratories have been studying the ability of different reagents and microbial nutrient systems to immobilize inorganics or destroy organics in the ground water and solid materials of an unconfined aquifer. The Department of Energy is sponsoring the research.

In the laboratory studies, completed in 1994, microbes exhibited the ability to degrade carbon tetrachloride and other chlorinated solvents when the redox potential was reduced to the point where nitrate or iron instead of oxygen acts as an electron acceptor. Chromate could be immobilized by reduction to highly insoluble chromium hydroxide or iron chromium hydroxide.

Bench-scale studies, completed in 1994, were intended to determine the nature of the reactions that occur and the efficiency with which they are induced by reagents or nutrients. The potential of cultured iron-reducing bacteria for remediating subsurface environments contaminated with carbon tetrachloride and chromium has been tested, and sodium dithionite was found to reduce structural ferric iron in Hanford soils, the planned area for a field demonstration. Further experiments indicate that the half-life of the dithionite ion is about two or three days in the Hanford confined aquifer. This half-life is adequate for reducing the contaminants in the plume, while ensuring that dithionite does not remain as a contaminant in the ground water for an extended time.

Wastes Treated: Chromium, chlorinated solvents

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Remediation with Zero-Valent Iron **Oregon Graduate Institute of Science and Technology**

Description of Research: The primary purpose of the research is to explain how iron degrades chlorinated solvents such as PCE, TCE, and carbon tetrachloride in ground water. Laboratory experimental systems and columns have been used to study the reaction between chlorinated methanes and their degradation by pure iron. The laboratory systems show that zero-valent iron participates in reductive dechlorination predominantly by direct reduction at the iron surface, a process similar to metal corrosion. Additional work has shown that iron reacts with nitro-aromatic groups, common in some types of munitions like TNT. Researchers are investigating the many conditions and complicating factors that affect remediation of chlorinated solvents and nitro-aromatic compounds using iron.

Wastes Treated: Chlorinated solvents, nitro-aromatic compounds

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References:

Agrawal, A. and Tratnyek, P.G. "Abiotic Remediation of Nitro-Aromatic Ground-Water Contaminants by Zero-Valent Iron." Preprints of Papers Presented at the 207th ACS National Meeting in San Diego, California, March 13-18, 1994. American Chemical Society, Division of Environmental Chemistry 34 (1), 1994, p 492-494.

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Permeable Chemical Reactive Barriers Rust Geotech, Inc.

Description of Research: For about 5 years, researchers at Rust Geotech, Inc. have been conducting laboratory batch and column studies of aquifer permeability, and two-dimensional tank and modeling experiments on chemical reactive barriers that sorb such elements as uranium, molybdenum, copper, lead, zinc, and radium. The primary purpose is to determine the applicability of chemical reaction barriers to in situ remediation of uranium tailings, which threaten ground water at many DOE mill sites. Some important areas under investigation are the sorption capacities for a variety of contaminants and the relative immobility of the sorbing phase under aquifer flow conditions. Tests have been conducted on barriers containing primarily low-cost materials such as hydrated lime, fly ash, barium chloride, calcium phosphate, titanium oxide, peat, lignite, ferric oxyhydroxide, ferrous hydroxide, hydrophobic zeolite, hydrated iron oxide, and ferrous sulfate. Extraction rates for uranium (initial concentration 30 mg/L) were greater than 99% using hydrated lime, fly ash, barium chloride, calcium phosphate, titanium oxide, peat, and lignite. More than 96% of the molybdenum (initial concentration 8.9 mg/L) was extracted by ferrous sulfate, ferric oxyhydroxide, titanium oxide, peat, hematite, calcium chloride, and barium chloride. The most extensive research effort has centered around the use of ferric oxyhydroxide to immobilize metals and uranium. The studies have shown that ferric oxyhydroxide (1) is an inexpensive sorbent for uranium and metals, (2) can be injected into ground water, (3) should remain immobile once emplaced, and (4) once emplaced, should not reduce aquifer permeability. All of these issues are important to the successful implementation of a subsurface reactive barrier.

Rust Geotech conducts its research at the Environmental Sciences Laboratory in Grand Junction, Colorado. This lab is part of the Department of Energy's Grand Junction Project Office.

Wastes Treated: Uranium, molybdenum, arsenic, copper, lead, zinc, cadmium, chromium, and radium

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References:

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Zeolites as Permeable Barriers **New Mexico Institute of Mining and Technology**

Description of Research: The Institute is developing a permeable barrier of altered zeolite that retains some major classes of ground-water contaminants while allowing ground water to pass through. The barrier is selective for major classes of soluble organics such as benzene and trichloroethylene, inorganic cations such as lead and cadmium, and inorganic anions such as chromate and arsenate. Raw zeolite, which has a high adsorptive capacity for positively charged contaminants, is treated with cationic surfactants that increase its ability to adsorb organics and negatively charged inorganic contaminants. The hydraulic properties of the surface-altered zeolite can be tailored for specific needs. Researchers are characterizing the properties of the altered zeolite and its stability and adsorptive characteristics as a function of environmental variables such as pH and temperature. Pilot scale tests in a permeable barrier system, and a field demonstration are planned.

Wastes Treated: Soluble organics, inorganic cations and anions

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References:

Bowman, R.S.; Flynn, M.; Haggerty, G.M.; Huddleston, R.G.; Neel, D. "Organo-Zeolites for Sorption of Nonpolar Organics, Inorganic Cations, and Inorganic Anions." *Proceedings of the Joint CSCE-ASCE National Conference on Environmental Engineering*, July 12-14, 1993, Montreal, Quebec, Canada, p 1103-1109.

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Hydrodehalogenation of Chlorinated Substances in Water **Department of Civil Engineering, Stanford University**

Description of Research: Catalytic hydrodehalogenation using palladium and hydrogen is showing promise in laboratory studies as a viable method for treating water contaminated with chlorinated hydrocarbons even in the presence of oxygen, nitrite, sulfate, and chloride. In other laboratory scale studies, the transformation of chlorinated organic compounds, such as tetrachloroethylene, by iron and manganese powders in buffered water and in landfill leachate is being investigated.

Wastes Treated: TCE, PCE, other chlorinated solvents

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References:

Schreier, C.G. and Reinhard, M. "Catalytic Hydrodehalogenation of Chlorinated Ethylenes Using Palladium and Hydrogen for the Treatment of Contaminated Water." accepted for publication in *Chemosphere*, June 14, 1995.

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Remedial Applications of Zero-Valence Metals **Martin Marietta Energy Systems and Oak Ridge National Laboratory**

Description of Research: Researchers have been conducting laboratory batch and column studies on zero-valent iron during the past 2 years to establish the feasibility of using the metal for dechlorinating organic solvents and removing radionuclides in situ at the Department of Energy's Paducah Gaseous Diffusion Plant. Success in treating ground water contaminated with trichloroethene and technetium have led to a plan to implement a year-long Superfund treatability study of ground water at the Plant. Additional research by this group involves laboratory investigations of bimetallic processes that increase

the dehalogenation reaction rate for TCE and improve the rate of dehalogenation of less-chlorinated compounds, such as dichloromethane. These studies are showing success.

Wastes Treated: TCE, DCE, Vinyl Chloride, and Technetium

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References:

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Ground Water Restoration with Iron Metal GE Corporate Research and Development

Description of Research: Researchers at GE Corporate Research and Development have been studying the process by which iron metal and other iron-bearing minerals degrade chlorinated solvents, such as TCE, DCE, and VC in water. This research was undertaken to gain a fundamental mechanistic understanding of the chlorinated solvent/iron corrosion process and to determine the factors that affect dechlorination rate and long-term performance in ground-water treatment.

Reduction of chlorinated solvents promoted by iron metal surfaces was studied in laboratory experiments and columns with particular emphasis on reaction rates, product mass balances, ground-water treatability, and characterization of iron metal surfaces. A well-instrumented pilot-scale column system was used to predict chemical and hydraulic lifetime of commercial iron filings and to demonstrate that target effluent concentrations could be attained. Aging effects, such as those caused by mineral precipitation and potential biofouling, were accelerated by using flow velocities much higher than those typical of ground waters. Researchers continue to investigate other factors that affect the design and operability of permeable walls or columns composed of iron metal and iron minerals.

Wastes Treated: Chlorinated solvents

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References:

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In Situ Permeable Reaction Wall Waterloo Centre for Groundwater Research, University of Waterloo

Description of Research: Extensive bench-scale, batch and column studies over the past four years show that zero-valent iron can enhance the degradation by abiotic reductive dechlorination of halogenated organic compounds. The University has tested fourteen chlorinated methanes, ethanes, and ethenes using a variety of metals. Substantial degradation rates were obtained using iron for all tested compounds except dichloromethane. Many degradation rates were several orders of magnitude greater than those reported in the literature for abiotic and biotic degradation. Bench-scale laboratory batch experiments and treatability column experiments conducted with sand aquifer material confirmed halogen degradation in the presence of iron. The success of these studies has led to the testing of above-ground and in situ applications of permeable reaction walls for remediating contaminated ground-water and to patents.

Investigators at the University are continuing to develop various in situ barrier treatment designs for a wide variety of common organic and inorganic ground-water contaminants including chlorinated solvents, petroleum-derived contaminants such as BTEX, metals, nitrate, and phosphate. Several prototype systems have been field tested, and designs for some full-scale systems have been developed.

It is expected that many of the new treatment barriers will be used with the Funnel-and-Gate™ system developed initially at the Waterloo Centre for Groundwater Research and further developed and marketed by Waterloo Groundwater Control Technologies, Inc. The various design options of the Funnel-and-Gate™ are intended to direct contaminant plumes to the reactive media and direct clean water around the plume.

Field demonstrations are planned on the following types of reactions for in situ treatment walls:

- Promote denitrification of nitrate in a contaminant plume emanating from a septic tank by using an organic carbon source;
- Promote biologically mediated, reductive dechlorination of selected solvents by periodic injection of a carbon-amended solution;
- Remove iron, sulfate, and heavy metals in ground water from mine tailings using chemically active organic carbon to promote sulfate reduction;
- Remove phosphate by precipitation using a permeable iron oxyhydroxide solid; and
- Remove electroactive metals, such as hexavalent chromium, using zero-valent iron.

The Waterloo Centre for Groundwater Research is part of Ontario's Centres of Excellence program, a government sponsored partnership with academia and industry.

Wastes Treated: Numerous organic compounds such as carbon tetrachloride, chloroform, TCE, PCE, and BTEX; as well as metals, nitrate, and phosphate

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References:

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Permeable Reactive Barriers Los Alamos National Laboratory

Description of Research: Researchers have evaluated the applicability of gel materials in barriers to enhance natural biologic communities and to test chemical tracers and remote monitoring of hydrologic systems. Investigators have used zeolite, silica gel, sand, bentonite, aluminum crosslink polyacrylamide, and peat in permeable barriers. Approaches to managing biologic communities on the margins of a site in combination with other barrier systems are being evaluated. Barriers used as part of post-closure monitoring systems serve to warn of impending contaminant migration.

Post-closure monitoring experiments will focus on the evaluation of water saturation and chemical transport using tracers such as common anions, soluble organic acids, semivolatile organic acids, fluorescein, chromium, EDTA, and toluene labeled with carbon-13 for the bio-barrier.

The first barrier and monitoring systems were installed in 1992. Field tracer tests were scheduled for completion in early 1994, however, Department of Energy funding was discontinued after the first year. The research was conducted in partnership with the Universities of Houston and New Mexico and the DuPont and Pfizer Chemical Companies.

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